

Introduction

Thermal poling of glasses is of interest because of a set of reasons. Poling leads to the breaking of central symmetry of initially isotropic glasses that allows the generation of second harmonic and the Pockels electro-optical phenomenon, as well as to the structuring of glass surface and the formation of optical waveguides and other structures on the surface of poled glasses. A powerful technique to study characteristics of materials, including glasses, is the broadband dielectric spectroscopy (BDS). We apply this technique to characterize behavior of differently poled glasses.

Experiment

We studied glasses poled in blocking anode configuration with two types of thin-film anodic and cathodic electrodes. For this we deposited 50 nm gold film on both surfaces (25x25 mm²) of 1 mm thick commercial soda-lime glass slides (see glass composition in Table) either onto virgin slide surfaces (AU samples) or onto the surfaces previously covered by 5 nm chromium sublayer (CRAU samples). The samples were thermally poled at 573 K under 400 V DC. After almost complete decay of poling current, poled samples were cooled down to room temperature, and then the applied voltage was switched off. BDS study was performed using Novocontrol BDS80 ultra-broadband dielectric spectrometer (Novocontrol Technologies GmbH und Co. KG, Germany) with a Novotherm-HT furnace in the frequency range $0.2 - 3 \times 10^5$ Hz and at temperature varying from room temperature to 700 K. The heating rate was 1 K/min.

Table 1. Chemical composition of the Menzel glass microscope slides ³⁵ .									
Oxide	SiO ₂	Na ₂ O	K ₂ O	CaO	MgO	Al ₂ O ₃	Fe ₂ O ₃	SO ₃	Other
wt%	72.20	14.30	1.20	6.40	4.30	1.20	0.03	0.30	0.07

Results and discussions

Temperature dependences of the real, Z_{n}' , part of the complex impedance Z* of the studied samples are presented in Fig.1 for several measuring frequencies. One can see that poling resulted in significant changes in the character of these temperature dependences, namely: in the appearance of steps and maxima whose positions move with a change in frequency.



Fig.1. Temperature dependences of Zp' of the initial glass (left), CRAU (middle) and AU (right) samples for several measuring frequencies.

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Electric properties of polarized layer in alkaline silicate glasses

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> To explain this it is sufficient to pay attention to the concentration profiles in poled glasses, which evidence the presence of two regions (layers) essentially differing in cation (charge carriers in glasses) concentrations. In poling with blocking anode, all positive charge carriers (cations) are known to leave the subanode layer for the glass bulk. Thus, any poled glass appears to be a typical bilayer structure. To calculate impedance of such structure one should consider a serial connection of the layers, that is, two parallel RC circuits connected in series. Having the complete information about the electrical properties of the initial and poled glasses and about the thickness of depleted layer, one can obtain information about the properties of the layer.

Expressions for the components of the complex permittivity of the polarized layer:

$$\varepsilon_{l}^{'} = \frac{d_{l}}{d} \cdot \frac{\left(\varepsilon_{g}^{''} \cdot \varepsilon_{c}^{'} - \varepsilon_{c}^{''} \cdot \varepsilon_{g}^{'}\right)}{\left(\varepsilon_{g}^{'} - \varepsilon_{c}^{'}\right)^{2} + \left(\varepsilon_{g}^{''} - \varepsilon_{c}^{''}\right)^{2}}, \qquad \varepsilon_{l}^{''} = \frac{d_{l}}{d} \cdot \frac{\left(\varepsilon_{g}^{''} \cdot \varepsilon_{c}^{''} - \varepsilon_{c}^{''} + \varepsilon_{g}^{''}\right)}{\left(\varepsilon_{g}^{'} - \varepsilon_{c}^{'}\right)^{2} + \left(\varepsilon_{g}^{''} - \varepsilon_{c}^{''}\right)^{2}}$$

Here, the subscript c refers to the whole structure that is the poled glass sample, I - to the poled layer, and g - to the initial glass. The thicknesses of the polarized layers dAU=530±60 nm and dCRAU=650±25 nm. The calculated temperature dependences of the permittivity and acconductivity of these layers are presented in Fig.2 for 0.2 Hz frequency. The permittivity and acconductivity of the polarized layers are very low in comparison with the initial glass, that should be expected, since most of the charge carriers have left these layers.



Fig. 2. Temperature dependences of permittivity and AC-conductivity at 0.2 Hz frequency of 650 nm thick polarized layer in CRAU specimen (a) and 530 nm thick polarized layer in AU specimen (b).

The permittivity and ac-conductivity of the polarized layer in the CRAU sample are several times higher than in the AU sample. Supposedly, this is because trivalent gold atoms effectively occupy non-bridging oxygen bonds remaining after positive ions have left the subanodic layer of the sample. This limits the number of free positions and increases the length of the jump that significantly reduce the value of glass conductivity.

The dielectric response of poled glass samples is mainly determined by the electric properties of the cations-depleted subanodic layers. The BDS-measured dielectric spectra of the poled samples almost coincide with the spectra of these layers, for the contribution of the sample bulk to the measured dielectric spectra is negligibly small. This gives an opportunity to reveal specific properties of these layers rather than ones of the glass sample bulk in the measurements.

The behavior of dc-conductivity and static permittivity (ϵ at zero frequency) of the layers can be estimated from the Cole-Cole diagram presented in Fig. 3. The diagrams for poled glasses clearly show the semicircles associated with the polarized layer and a part of the semicircle associated with the relaxation process in the rest of the sample (initial glass).



the real part of dielectric permittivity of the polarized layer.

In the temperature range up to 500 K, the diagrams are superimposed exactly one on the other, and as the temperature rises, we are able to see an increasing part of the semicircle (more pronounced for CRAU sample). It means that in this temperature range the capacitance of the layer does not change, and only its resistance (conductivity) changes. Frequency, ω , corresponding to the maximum loss for a given temperature, is equal to $(RC)^{-1}$ ($\omega = 1/RC$) where R is the resistance of the layer, C is the capacitance of the layer at a given temperature. Estimating the value of static permittivity from the Cole-Cole diagrams, we obtain the temperature dependences of the dc-conductivity of the layers are shown in Fig. 4 in Arrhenius coordinates. The activation energies are almost the same and equal to 0.88-0.89 eV. Given the value of the found activation energies, charge carriers could be sodium ions.



Conclusions

The permittivity and ac-conductivity of polarized subanodic layer are very low compared to the initial glass. This should be expected because the most of the charge carriers have left subanodic region of the poled glass. It is found that electric properties of the layer are essentially conditioned by the structure of anodic electrode used in glass poling. It is also shown that dielectric response of poled glass samples is mainly determined by the electric properties of the cations-depleted subanodic layers. The dc conductivity of the depleted layer of glass in the case of the anodic electrode with chromium sublayer proves to be about an order of magnitude higher compared to the case of the gold electrode without the sublayer. But the activation energies of the charge carriers in these depleted layers turns out to be about the same and equal to 0.88-0.89 eV. Difference in the absolute values of conductivity when activation energies do not differ can be explained by the presence of gold ions which can penetrate into the glass and block free position for charge carriers' migration. Given the value of the found activation energies, charge carriers could be sodium ions.



Fig. 3. Cole-Cole diagrams for AU (left) and CRAU (right) samples for several temperatures. The inset in the left panel illustrates the coincidence of the Cole-Cole semicircles in the temperature range below 500 K, which evidences the absence of changes in the capacity and, respectively, in

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