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CRYSTALLIZATION OF POTASSIUM TITANOSILICATE GLASS UNDER THERMAL POLING USING A PROFILED ANODE

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Abstract: This paper is devoted to in-depth study of the crystallization process in the K_2O-TiO_2-SiO_2 glass under thermal poling using a profiled anode and heating temperature below the glass transition temperature. The crystallization was investigated by Raman scattering and mechanical profilometry at the specified conditions. It was found that the glass remained transparent without crystallization signs on the electrode-glass contact surface (profile peaks at the electrode) whereas the glass surface became frosted over other areas where there was an air gap between the electrode and glass (it was shown to be caused by the formation of a nanocrystalline anatase layer). A transition zone a few tens of micrometers wide and a few micrometers high was formed between frosted and transparent glass areas, i. e. at the edges of the electrode-glass contact surface. The mechanism of formation of the crystalline phase and relief was discussed.

Keywords: glass, thermal poling, profiled anode, crystallization, Raman scattering

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КРИСТАЛЛИЗАЦИЯ КАЛИЕВО-ТИТАНОСИЛИКАТНОГО СТЕКЛА ПРИ ТЕРМИЧЕСКОЙ ПОЛЯРИЗАЦИИ С ИСПОЛЬЗОВАНИЕМ РЕЛЬЕФНОГО АНОДА

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Аннотация. Работа посвящена детальному анализу процесса формирования кристаллических структур в стекле системы K_2O-TiO_2-SiO_2 при полинге с использованием рельефного анода и температуры нагрева ниже температуры стеклования. Кристаллизация стекла при указанных условиях изучена методами комбинационного рассеяния света и механической профилометрии. Обнаружено, что в областях механического контакта электрода со стеклом (выступы профиля на электроде) стекло остается прозрачным без признаков кристаллизации, тогда как в остальных областях, где между электродом и стеклом существует воздушный промежуток, поверхность становится матовой (показано, что это вызвано образованием слоя нанокристаллического анатаза). Между матовой и прозрачной областями, т. е. на краях областей контакта с электродом, формируется переходная область шириной несколько десятков микрометров и высотой несколько микрометров. Обсуждается механизм образования кристаллической фазы и рельефа.

Ключевые слова: стекло, термическая поляризация, профилированный анод, кристаллизация, комбинационное рассеяние света

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Introduction

The procedure for thermal polarization of glass in an electric field is commonly referred to as thermal poling. This procedure consists of heating a glass plate about 1 mm thick (placed between two metal electrodes or other Class 1 conductors) to a temperature sufficient for activating pronounced conductivity, subsequently applying a DC potential of the order of several hundred volts to the electrodes. The heating temperature for standard soda lime glasses is 250–300 °C, which is significantly lower than the glass transition temperature equal to approximately 550 °C. As the electric field forces the most mobile, positively charged cations (alkali metal ions) to drift from the surface into the bulk of the plate, the composition and structure of the subanodic region of the glass are modified, and a layer of negative space charge appears, generating a strong electric field [1–3].

It is well known that the electric field exerts a considerable influence on the thermodynamics and kinetics of such processes in nanocrystals as phase separation, nucleation and growth, which may serve to either enhance or inhibit crystallization [4–7], in particular by altering the crystalline motifs of the glass [8]. Several papers reported on the surface crystallization of glasses observed under poling and subsequent heat treatment at temperatures above the glass transition: crystallization of barium titanate ($BaTiO_3$) in BaO-TiO_2-TeO_2 system glasses [9], as well as crystobalite (SiO_2) [10], monoclinic dicalcium silicate (β-Ca_2SiO_4) and diopside ($CaMgSi_2O_6$) in silicate glasses [11, 12]. Crystallization of anatase (TiO_2) was also detected in K_2O-TiO_2-SiO_2 system glass under poling below the glass transition temperature but without the additional heat treatment [13] commonly used to produce crystalline nuclei in the glasses [14].

The goal of this study consisted in detailed analysis of the evolution of crystalline structures in K_2O-TiO_2-SiO_2 system glass under poling using a patterned anode at a heating temperature below the glass transition.

Patterned electrodes providing local crystallization of glass under poling offer an alternative to the laser irradiation method generally used to induce local crystallization. We selected a coin to illustrate local crystallization for a surface relief of an imprinted electrode with a rather complex structure.

Crystallization was analyzed by Raman spectroscopy (RS) using a spectrometer equipped with a confocal microscope; the morphology of the glass surface was studied with a mechanical profilometer.

Experimental

The experiment was performed with 4 mm thick plates of commercial LF9 glass with a glass transition temperature T_g = 485 °C and the composition given in Table.

Table

Composition of the glasses used in the experiment

Chemical composition, mol%					
SiO_2	TiO_2	K_2O	Al_2O_3	B_2O_3	As_2O_3
61.80	16.63	16.33	2.06	3.00	0.18

The anode electrode was a coin 16 mm in diameter with a relief height on the surface of the pattern equal to 15 μm. Poling for 60 min was carried out in air at a DC voltage of 850 V and a temperature of 440 °C. The charge that passed through the sample during poling amounted to 3.7 C. The RS spectra were excited with a continuous laser operating at 532 nm and recorded using a Witec Alpha 300R spectrometer equipped with a confocal microscope. The morphology of the sample surface was analyzed with a mechanical Ambios XP-1 Stilus Profiler.

Results and discussion

Fig. 1,*a* shows an optical image for a fragment of the coin imprinted on the glass subjected to poling. The imprint mirrors the pattern on the coin (digits '2006'); the glass remains transparent in the regions where it contacts the protrusions on the coin surface and outside the coin, while the surface becomes frosted in other regions under the coin.

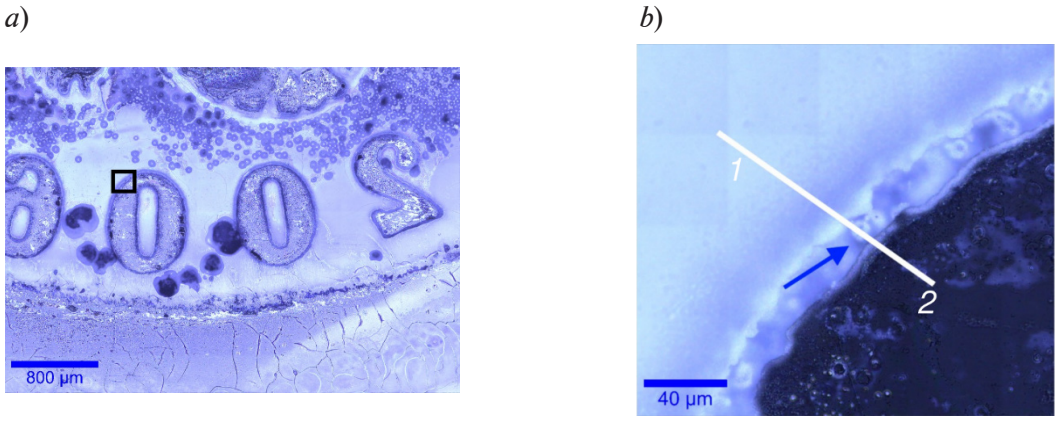

Fig. 1. Optical images of coin fragments imprinted on glass subjected to poling; data are presented in different scales: Fig 1,*b* corresponds to a fragment of glass surface near the digit '0', marked by the square in Fig. 1,*a*. The white line between the frosted (*1*) and transparent (*2*) regions corresponds to the scan line (see Figs. 2–4); the arrow indicates the transition region between *1* and *2*

Fig 1,*b* corresponds to a fragment of glass surface near the digit '0', marked by the square in Fig. 1.*a*. Fig. 1.*b* also shows a transition region containing optical inhomogeneities.

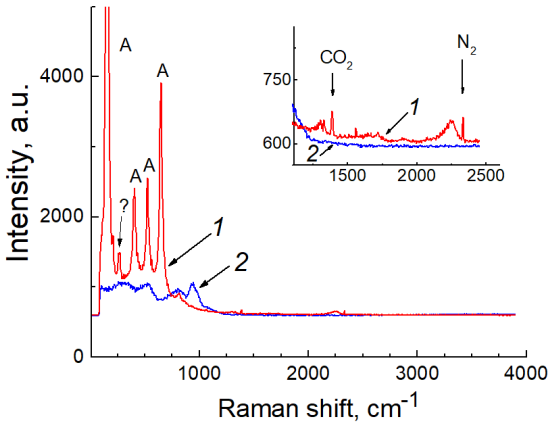

Fig. 2. RS spectra measured in the frosted (*1*) and transparent (*2*) regions of poled glass (see Fig. 1,*b*): peaks of nanocrystalline anatase (A) and lines of atmospheric gases (in the inset) are visible

Fig. 2 shows the RS spectra measured in the frosted (*1*) and transparent (*2*) regions (non-contacting and contacting, respectively, see Fig. 1,*b*).

Spectrum *2* in Fig. 2 is typical for potassium titanosilicate glasses and contains the following broad bands, cm^{-1}:

250–350, 450–550, 700–800,
900–1000, 950–1050;

among these, the bands at 450–550, 950–1050 cm^{-1} correspond to Si–O bonds, and the rest to Ti–O bonds. The bands at 700–800 and 900–1000 cm^{-1} are associated with octahedral and tetrahedral coordination of titanium ions, respectively [15]. Spectrum *1* in Fig. 2 contains several narrow lines belonging to nanocrystalline TiO_2, as well as one line of an unidentified impurity phase (labeled by a question mark) and lines of trace species (see the inset in Fig. 2) [16, 17]. The positions of the lines corresponding to nanocrystalline anatase on the frequency scale and their widths depend on the average size of nanocrystals as well as on the mechanical stresses in the glass [16].

Notably, monocrystalline anatase has six Raman-active fundamentals, cm^{-1} [17]:

144 (E_g), 197 (E_g), 399 (B_{1g}), 516 (A_{1g}), 519 (B_{1g}) and 639 (E_g).

The position of the most intense spectral line of anatase (144 cm^{-1}) and its width (15 cm^{-1}), which depends on the size of the structure where Raman scattering occurs, can be used to estimate the average size of nanocrystals (without taking into account the mechanical stresses) [16].

According to the estimates in [16], the position of the line equal to 150 cm^{-1} corresponds to an average nanocrystal size of 7–10 nm for a spectral width of 15 cm^{-1}. In our case, we can assume that the size of the nanocrystals lies in approximately the same range.

Analyzing the RS spectra in Fig. 3, obtained by scanning the surface along the straight line between the regions *1* and *2* (see Fig. 1,*b*), we can conclude that crystallization occurs before the edge of the digit '0' (including the transition region), where the crystalline phase is represented by TiO_2; after this border is crossed, the glass does not contain signs of crystallization. Notably, no crystallization is observed outside the coin. Surface morphology studies indicate that the transition region forms along the edges of each imprinted digit and consists of protrusions several tens of micrometers wide and several micrometers high.

Fig. 4 shows as an example a profile of the glass surface in the transition region at the border of the digit 0 obtained by a mechanical profiler. Evidently, the transition region is a protrusion about 45 μm wide and 1.5 μm high in this case. Our experiments have revealed that neither a relief nor a crystalline phase are produced under heat treatment in the same mode and using a coin but without applying an electric field.

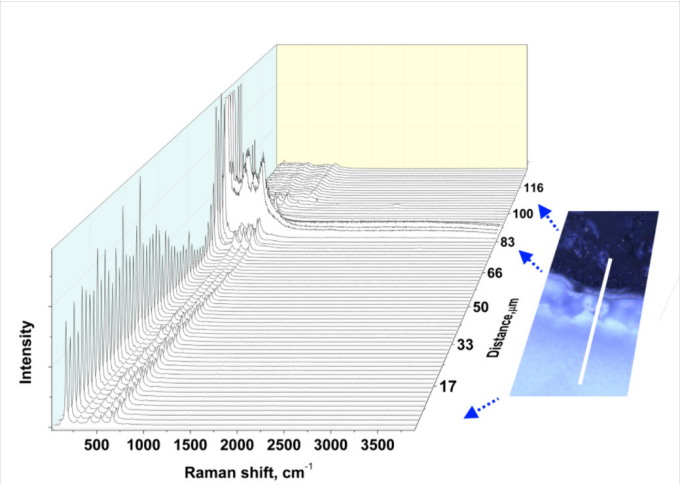

Fig. 3. RS spectra in poled glass for surface scans along a straight line between regions *1* and *2* (see Fig. 1,*b*). Scanning step and range are shown

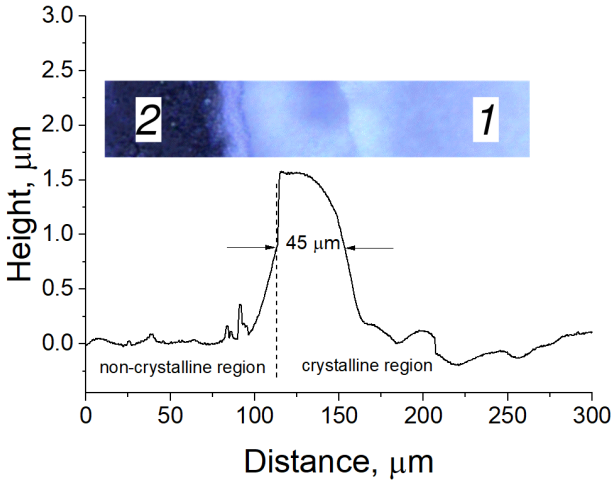

Fig. 4. Surface profile of poled glass in the transition region at the borders of the digit '0' (see Fig. 1,*b*), obtained with a mechanical profiler

We can offer the following explanation for the results obtained. The electric field is applied to the entire region under the coin (electrode) during poling, reaching the highest values in the region where the electrode directly contacts the glass. Alkaline ions from the near-surface region migrate deep into the glass, so that the composition of the glass changes: instead of alkaline ions drifting deeper under the influence of an electric field, hydronium ions (H_3O^+) are injected into the glass from the ambient. Interestingly, hydronium penetrates the region where the electrode contacts the glass less effectively than the region outside the contact. As alkaline ions are removed from the near-surface layer, the ternary $K_2O-TiO_2-SiO_2$ system observed near the glass transition is transformed into a binary TiO_2-SiO_2 system falling into the region of metastable liquid-liquid phase separation (LLPS). It is known that the region below the liquidus occupies almost the entire range of the compositions in the TiO_2-SiO_2 system [18], so that introducing even a small amount of titanium oxide into the silicate system triggers the metastable LLPS. Phase separation into silicon and titanium oxides, as well as crystallization of the latter follow the mechanism of diffusion-controlled phase decomposition within the metastable LLPS region. The crystallization process is affected not only by temperature but also by the molar ratio of the oxides (the higher the silicon oxide content, the higher the required temperature) [19, 20].

In this case, a third parameter, namely, the electric field strength, is added to temperature and molar ratio of oxides. As already noted, the electric field can both enhance and inhibit the phase separation and crystallization processes [4–7]. These processes are enhanced in the TiO_2-SiO_2 system, and the viscosity of the glass is reduced, which may lead to a decrease in the crystallization temperature. Crystallization is likely preceded by LLPS because the surface becomes frosted and starts to scatter light strongly. Strong scattering is due to the large difference in refractive indices between the SiO_2 ($n = 1.46$) and TiO_2 ($n = 2.55$) phases.

In this case, TiO_2 develops under poling at 440 °C, while it only appears at temperatures above 600 °C under thermal annealing of binary TiO_x-SiO_{1-x} glasses ($x = 0.20-0.65$) and films of similar composition ($x = 0.15-0.90$) [19, 20]. The question here is why crystallization is observed at the glass-air interface and is absent at the glass-anode interface. We believe that the difference in the kinetics of ion diffusion at these interfaces plays a central role in this case, because, as it is easier for hydronium to penetrate the glass-air interface, this largely serves to reduce the glass transition temperature, which promotes crystallization. Therefore, the glass does not have sufficient time to crystallize in the experimental conditions due to the low crystallization rate in the region where it contacts the electrode. Our experiments indicate that if the temperature is increased to 460 °C (instead of 440 °C) with the same poling voltage and duration, crystallization extends to the entire region under the coin; this confirms the role played by the kinetic factor in the crystallization process.

Now let us discuss the hypothetical mechanism causing protrusions to appear on the surface of the glass near the interface with the region where it contacts the electrode. The protrusions forming point to a local increase in the glass volume of glass within the given region. The increase in the glass volume is observed as ions with a smaller radius are replaced by ions with a larger radius, for example, during ion exchange, when sodium ions are replaced by potassium ions [21] or during hydrothermal treatment of glass, when vapor bubbles are formed in it [22–24].

It was established in [22–24] that the glass transition temperature T_g of the glasses subjected to hydrothermal treatment is highly dependent on the water content and can decrease to $0.8T_g$ at 1–2 wt.% H_2O and to $0.5T_g$ at 10 wt.% (the temperature T_g is measured in °C). This, in turn, leads to a decrease in the crystallization temperature and a decrease in the viscosity of the glass, additionally affecting the phase separation of vapor [25].

Water vapor bubbles appear in the glasses prepared by the hydrothermal method under annealing at a temperature above the glass transition (as already noted above), and the volume of the glass increases substantially as a result (glass foaming). Therefore, hydrothermal treatment can be used to synthesize porous glasses (see [26] and references therein). Water can also condense in the near-surface region of the glass under poling. The negatively charged non-bridging oxygen atoms O^-, remaining after potassium cations escape, react with H_3O^+ to produce water:

$$\sim Si{-}O^- + H_3O^+ \rightarrow \sim Si{-}OH + H_2O.$$

Replacing potassium cations with hydronium ions cannot lead to an increase in the volume of the glass because of the slight difference in their ionic radii; however, if the glass transition temperature decreases due to increased water content accompanying the penetration of hydronium and turns out to be below the poling temperature, regions with high hydronium contents may favor the generation of vapor bubbles. Since the electric field reaches maximum strength along the perimeter of the electrode relief (edge effect), bubble generation is the most effective along the perimeters of the digits. The most likely reason why protrusions appear on the glass is that vapor bubbles are generated along the borders of the digits.

Thus, a considerable decrease in the glass crystallization temperature with TiO_2 evolving in the near-surface region of the glass under poling can be explained by the effects of the electric field and the water formed in the glass on the thermodynamics and kinetics of crystallization, while the process itself can be characterized as surface crystallization in the electric field.

Conclusion

Considering the poling of $K_2O-TiO_2-SiO_2$ glasses at temperatures below the glass transition of the material with the initial composition and using a patterned anode (imprint), we have discovered that crystalline structures from anatase (TiO_2) nanocrystals, mirroring the pattern on the anode, develop on the surface of the glass. Protrusions appear at the interface between non-crystalline and crystalline regions.

Our findings may be of interest to researchers in the structures with photocatalytic properties and coatings with anatase nanocrystals on the surfaces of titanosilicate glasses.

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