To the issue of the second harmonic generation in poled silicate glasses

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Abstract. Thermal relaxation of the second harmonic generation (SHG) observed in thermally poled soda-lime silicate glass is studied. At least two relaxation processes could be distinguished. Determined activation energy of the fastest SHG relaxation process is equal to about 0.5 eV. This SHG relaxation occurs at temperatures essentially below ones, at which the thermally stimulated depolarization current (TSDC) measurements show the relaxation of the spatial charge formed in thermal poling of the glasses. This confirms that SHG in poled glasses is not mostly conditioned by the “frozen” spatial charge and electric field of this charge.

1. Introduction
Thermal poling (polarization) of silicate glasses is known to result in structural and compositional changes in their subsurface layer. Poled glasses also demonstrate properties of anisotropic optical media: linear electrooptic effect, second harmonic generation (SHG), etc. [1,2] which are of interest for optoelectronics. According to the prevalent point of view [3], the anisotropy originates in the static electric field created by the spatial electric charge formed in glasses in poling and “frozen” after their cooling. However, in the previous study [4], we have demonstrated that in the heating of poled glasses the complete relaxation of the SHG signal precedes the spatial charge relaxation process which takes place at essentially higher temperatures and is confirmed by the TSDC (thermally simulated depolarization current) measurements. Here we present the studies of the kinetics of the SHG relaxation.

2. Experimental and results
A soda-lime glass slides “Menzel” purchased from Agar Scientific were used in this research. The glass composition is presented in Table 1.

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

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

In the thermal poling experiments, each glass sample 25x30x1 mm³ in size was pinched between grinded carbon cathode and rough silicon anode in the polarization block. We placed a 100 µm thick
lining ("Menzel" cover glass) between the sample and cathodic electrode to prevent deposition of \( \text{Na}_2\text{O-}\text{SiO}\cdot n\text{H}_2\text{O} \) film on the cathodic surface of the sample, because such film could interfere with correct SHG measurements. In our poling experiments, this film formed on the cathodic surface of the lining that was removed before SHG measurements. Then the polarization block was heated in a furnace up to 300 °C and 1 kV DC voltage was applied for 40 min. After the poling, the sample was cooled down to room temperature under the voltage applied.

The voltage provokes the drift of thermally activated cations towards the cathode. This results in spatial charge formation in such a way that the electric field generated by this charge starts to compensate the external electric field applied, so that the polarization current decreases. Temporal dependences of the polarization current of 5 prepared samples are presented in figure 1.

![Figure 1](image1.png)

**Figure 1.** The dynamics of polarization current of 5 samples polarized at 300 °C under 1 kV.

The intensity of the SHG signal in poled sample was measured using Maker fringes technique [6]. The experimental layout for SHG intensity measurements is shown in figure 2.

![Figure 2](image2.png)

**Figure 2.** Experimental layout for SHG measurements. The spectra near the filters represent their transmittance.
Every studied sample was fixed at the angle $63^\circ$ relative to the incidence laser beam that provided maximal SHG signal. The isothermal kinetics of the signal relaxation (decay) in the temperature range $150 – 190$ °C (with $10$ °C step) was recorded (see figure 3).

![Graph showing normalized SHG signal vs time for different temperatures (150°C, 160°C, 170°C, 180°C, 190°C).](image)

**Figure 3.** SHG relaxation at different temperatures.

The character of the kinetic curves in figure 3 evidences in favour of at least two processes taking place in the SHG relaxation. Thus, it appears that the relaxation process can be described by the sum of two exponential functions:

$$I(t) = I_1 e^{-\frac{t}{\tau_1}} + I_2 e^{-\frac{t}{\tau_2}},$$

where $I$ is the SHG intensity, $I_1$ and $I_2$ are the constants, $t$ is the time, $\tau_1$ and $\tau_2$ are the relaxation times of the first and the second relaxation processes, respectively. From figure 3 it follows that the relaxation time of the second (slow) process, $\tau_2$, is much higher than the one of the first (fast) process, $\tau_1$. For rough evaluation of $\tau_1$ at different temperatures, we neglected the presence of the slow process for time $<1000$ sec and approximate relaxation kinetics in this time interval using a single exponential function. We evaluated the activation energy of the fast process, $W$, using the Arrhenius graph: $\ln(\tau)$ vs $1/T$, where $T$ is the temperature:

$$W = k \times \frac{d(\ln\tau)}{d(\frac{1}{T})},$$

where $k$ is the Boltzmann constant. This graph is shown in figure 4, and calculated activation energy is equal to $\sim0.5$ eV.

One can see from figure 3 that at different temperatures SHG relaxation curve have different horizontal asymptotes, i.e. different levels of SHG signal after the annealing. We assume that this can be related to the different contribution of unpolarized glass surface nonlinearity to the SHG signal at different temperatures. To verify this, we measured the SHG signal originating in the surface nonlinearity in the course of fast linear heating and subsequent cooling of an unpolarized glass, see figure 5.
Figure 4. Temperature dependence of the relaxation time of the fast process: red line is the result of the approximation with linear function; numbers near the points are the values of calculated relaxation times in sec.

Figure 5. SHG signal from the unpolarized glass at different temperatures.

Figure 5 indicates that the SHG signal from the surface nonlinearity of the unpolarized glass decreases with heating. This allows concluding that different asymptotes of the SHG signal for longer annealing could be explained by different contributions of surface nonlinearity.

3. Discussion

SHG relaxation curves shown in figure 3 correspond well to a single exponential function in the first 1000 sec time interval. Evaluated activation energy of this fast relaxation process which dominates in this time interval is equal to ~0.5 eV. It is worth noting that in accordance with TSDC study [7], the
main relaxation of “frozen” spatial charge (charge carriers redistribution) is negligible in the temperature range used in the present research, and the main relaxation of the spatial charge takes place above the glass transition temperature with activation energy is ≥ 3 eV. In fact, in the temperatures below 200 °C, TSDC, that is, thermally simulated depolarization current, is extremely low and hardly measurable. Thus, the present research allows supposing that the appearance of SHG signal in poled glasses is not mostly conditioned by the spatial “frozen” charge and electric field generated by this charge. By now, the microscopic mechanism of the SHG relaxation process characterized by activation energy 0.5 eV is not identified.

The experimental results presented in figure 5 raise a question: what is the process that could provide surface nonlinearity that varies with temperature? The study [8] indicates that the latter could be due to the desorption of the ions (or molecules) adsorbed on the glass surface. This assumption can explain the observed (see figure 5) decay (in heating) and (in cooling) recovery of the SHG signal from the unpolarized glass. This can be due to the adsorption/desorption of water vapor from ambient atmosphere on the glass surface.

4. Conclusion

Thus, the performed studies allow concluding that only a negligible part of the charge carriers redistributed in the bulk of the thermally poled glass and forming the “frozen” spatial charge is responsible for the SHG. Measurements of SHG signal from the unpolarized glass at different temperatures indicate that the process of water adsorption/desorption on the glass surface influences the second harmonic generation and decay.

Acknowledgments

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