Second harmonic generation and charge relaxation of poled glasses

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Abstract. We measured thermal relaxation of the second order nonlinearity (SON) observed in a thermally-poled soda-lime silicate glass. It is shown that 50-min annealing of the glass at 400°C results in a complete SON degradation. Performed studies of thermo-stimulated depolarization current (TSDC) revealed that the poling-induced spatial electric charge relaxes above the glass transition temperature. This indicates that SON is not induced by this spatial charge.

1. Introduction

Studies of thermally-polled multicomponent silicate glasses are of interest due to the appearance of second order nonlinear optical phenomena, such as the second harmonic generation (SHG) after poling [1], contrary to virgin glasses. These effects could find applications in micro- and nanophotonics, integrated optics and others. It is a common point of view that the formation of a spatial electric charge in the course of the thermal poling and “frozen” electric field generated by this charge are responsible for the SHG [2]. In our previous studies, it has been found that the relaxation of the most of spatial electric charge, which was formed in the glass by poling, takes place above the glass transition temperature [3]. Here we present the data on the SHG relaxation and the spatial charge relaxation based on thermally stimulated depolarization current (TSDC) spectra [4]. These provide the information about the relation of the processes occurring in the course of the thermal poling and the origin of the optical nonlinearity observed in thermally-poled glasses. In this paper, we show that the spatial charge relaxation and the observed SHG relaxation are independent processes.

2. Experimental

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    |

The polarization of 1 cm thick glass slides was performed at 300°C for 50 min under DC electric voltage of 1 kV. After the poling, the samples were cooled down to room temperature under the voltage applied and voltage was off. Experimental layout for thermal poling is shown in fig. 1. We used stainless steel electrodes with 10x20 mm² area pressed to the glass surface.
Figure 1. Experimental layout for thermal poling: R⁺ - univalent cation, R²⁺ - bivalent cation, O – oxygen, Si – silicon, E_{ext} – external electric field.

Under the voltage applied, thermally activated alkali and alkali-earth cations move toward cathode from the anodic side of the glass. This results in the formation of a spatial charge, which electric field finally compensates the external field generated by the electrodes, and, as the result, the current through the glass drops. This process is characterized by the glass polarization curve (fig.2). After cooling under the voltage applied the spatial charge became “frozen” and does not relax because of the kinetic restrictions.

Figure 2. Polarization curve obtained from 1 kV, 300 °C poling.

The magnitude of SHG in the poled glass sample was evaluated using Maker fringes technique [6]. The experimental setup used to characterize the SHG is shown in fig.3. After measuring the Maker curve using 1064 nm wavelength laser generating 10 nm pulses, we fixed the angle of the laser beam incidence at the sample equal to 63 °, which provided maximal SHG signal magnitude. Then we heated this sample to 400 °C and measured time dependence of the SHG signal, that is, its relaxation (see fig. 4(a)). As seen, the SHG signal has almost completely relaxed in ~50 minutes and dropped down to the SHG signal generated by the surface of non-poled glasses.
Figure 3. Experimental set-up used for the SHG measurements. The spectra above the filters represent their transmittance.

Figure 4. SHG relaxation: (a) at 400 °C, (b) at 275 °C.

The study of the SHG relaxation at temperature of 400 °C have shown that the decay of the SHG signal obeys the first-order kinetics (fig 4 a), with relaxation time being equal to about 34 minutes.

Similar measurements performed with the sample under annealing at lower temperature, 275 °C, have shown that the process of the SHG relaxation cannot be described by one relaxer only (see fig. 4(b)). In the relaxation at 275 °C, contrary to the anneal at 400 °C, one can observe that there is a process, which cannot be registered at 400 °C, for at this temperature it is much faster.

To characterize the spatial charge relaxation (glass depolarization when the shifted positive charge carriers move back towards the anodic side of the glass and compensate negative charges formed in the poling process) we have performed TSDC characterization of the poled and then annealed at 400 °C glass sample. The schematic of the measurements and the measured TSDC are shown in fig. 5. The TSDC was recorded at heating rate of 10 °C/min. We used graphite electrodes pressed to the glass surface.
3. Discussion
The TSDC of the annealed at 400 °C glass sample, where the SHG has completely degraded, reveals the spatial charge relaxation peak at 640 °C and then an increase in the relaxation current, which starts at ~700 °C. This indicates that the SHG in the poled glass is not directly related to the spatial charge, which relaxes under the secondary heating of the glass above the glass transition temperature (530 °C [5]).

4. Conclusion
Our experiments have shown that 50-min annealing at 400 °C results in the disappearance of SHG in the poled soda-lime glass sample with the SHG relaxation time of ~34 min. The TSDC through this sample shows the independence of the poling-induced spatial charge relaxation and the second harmonic generation relaxation. These relaxation processes occur at essentially different temperatures due to a difference in their relaxation times.

Acknowledgments
This work was supported by Russian Science Foundation, grant #16-12-10044-P.

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