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THERMAL RELAXATION OF OPTICAL NONLINEARITY IN THE POLED GLASSES

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The thermal relaxation of second-order optical nonlinearity in the subsurface layer of a poled soda-lime silicate glass has been studied. The glass annealing below glass transition temperature was shown to lead to full relaxation of the nonlinearity. At the same time, the measurements of thermostimulated depolarization current demonstrated that spatial electric charge formed in the course of the glass polarization relaxed above the glass transition temperature. This allowed concluding that the second-order optical nonlinearity in the poled glasses was not induced by the spatial electric charge.

Keywords: glass, optical nonlinearity, polarization, poling, relaxation, depolarization, thermostimulated depolarization current

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Introduction

Second-order nonlinear optical phenomena (such as second harmonic generation (SHG)), which are observed in multicomponent glasses after their thermal polarization [1, 2], are of clear scientific interest to researchers, and in addition, can find commercial application in photonics, integrated optics, etc. For this reason, studies of thermal relaxation of optical nonlinearity in poled glasses are very relevant today.

Most publications on this problem (see, for example, [3, 4]) associate the appearance of SHG in poled glasses with the fact that a spatial electric charge is formed in glasses during polarization, which in turn creates a 'frozen' electric field in the glass volume. This field leads to breaking of the initially isotropic (centrosymmetric) glass structure, i.e., the latter becomes anisotropic, and the glass itself acquires properties of uniaxial crystals exhibiting second-order optical nonlinearity. However, it was established recently [5] that relaxation of the main part of the spatial electric charge formed in glass during its polarization occurs at temperatures above the glass transition temperature.

In this paper, we present the results of studies comparing the kinetics of SHG relaxation with the data on spatial charge relaxation obtained from measurements of thermally stimulated depolarization currents (TSDC) spectra [6].

These comparative studies were aimed at expanding our understanding of the correlation

Table

Composition of industrial alkali silicate glass

Chemical composition, wt%						
SiO_2	Al_2O	Na_2O	K_2O	MgO	CaO	Other oxides
72.2	1.2	14.3	1.2	4.3	6.4	0.33

between the processes occurring during glass polarization and the appearance of optical nonlinearity in poled glasses. However, spatial charge relaxation and SHG relaxation were found to be independent processes.

Experimental

Industrial alkaline-silicate glass purchased at Agar Scientific (Menzel Gläser slides) was used in this study. The glass composition is given in Table, the glass transition temperature of this object was 530°C [7].

The samples had a thickness of 1 mm. Polarization was carried out at 300°C for 50 min at a constant voltage of 1 kV. After polarization, the samples were cooled to room temperature under applied voltage, after which the voltage was turned off. A schematic of the glass polarization experiment is shown in Fig. 1. We used 10×20 mm stainless steel electrodes pressed against the glass surface.

At this temperature, the mobility of alkaline and alkaline earth cations contained in glass increases so much that the applied electric field forces these cations to shift noticeably towards the cathode [8, 9], with a spatial charge formed as a result. As noted above, the presence of a spatial charge generates an electric field that compensates the external applied field, and the current through the glass decreases. A typical dependence of polarization current on time is shown in Fig. 2. After cooling to room temperature under the applied voltage, the spatial charge 'freezes' in the glass and can no longer disappear (relax) due to kinetic limitations, i.e., extremely low mobility of cations at room temperature.

The SHG efficiency in samples of poled glasses was determined by Maker's fringe method [10]. The scheme of measurements used to determine the SHG characteristics is shown in Fig. 3. We measured the signal of the second harmonic emission of the Litron Nano L laser operating at 1064 nm and generating pulses with a duration of 6 ns. The incidence angle of the laser beam on the sample was equal to 63° and fixed, corresponding to the maximum value of the SHG signal. Fig. 3 also shows the full Maker picture obtained in poled glass, from which it can be seen that the the SHG signal indeed reaches maximum at an angle of 63°.

The figure also shows the measured dependence of SHG on the angle of rotation of the sample relative to laser radiation

Poled glass samples were subjected to isothermal annealing at two temperatures (275 and 400°C). The SHG signal level was measured

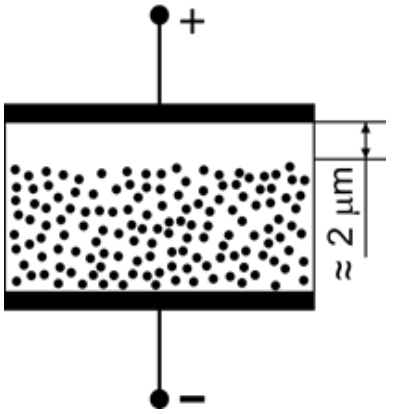

Fig. 1. Scheme of glass polarization: polarization voltage $U \approx 300$ V, polarization temperature $T \approx 250$°C, electric field in the depleted layer formed $E \approx 0.2$ V/nm.
The dots correspond to mobile cations in the sample; its region about 2 μm thick becomes depleted of mobile cations after polarization

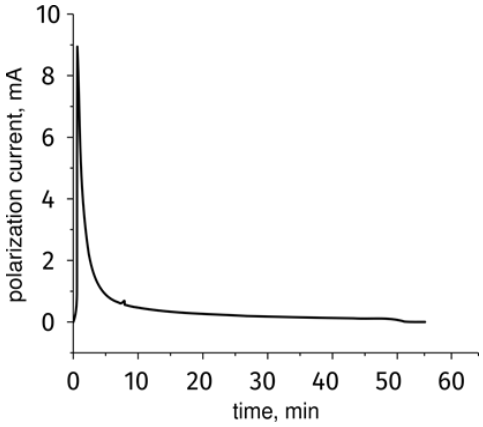

Fig. 2. Typical time dependence of polarization current in the sample glass

during annealing, i.e., the kinetics of isothermal SHG relaxation was determined.

After annealing, TSDC spectra were measured over a wide temperature range (from room temperature to glass transition temperature and higher). These spectra should either point to complete relaxation of the spatial charge after annealing at temperatures below 400°C (absence of any peaks) or determine the region of temperatures where relaxation of the 'frozen' spatial charge actually occurs, i.e., the charge carriers generating the electric field in the bulk of the glass move back to the anode region.

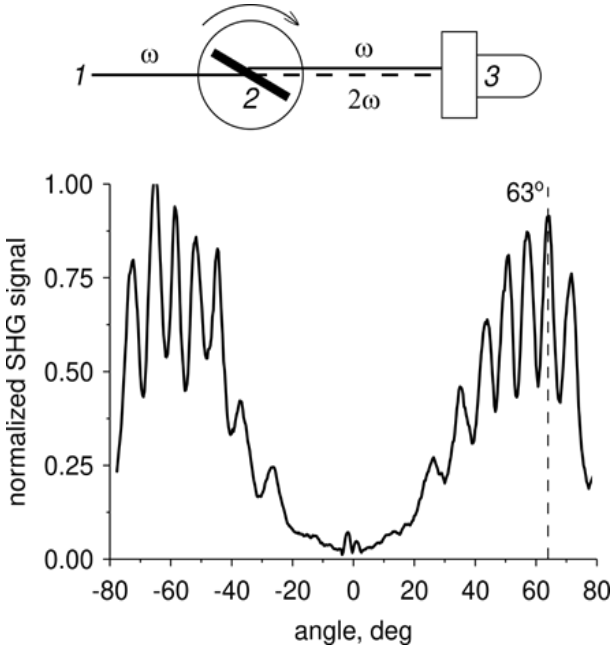

Fig. 3. Schematic for measurement of SHG efficiency in poled glasses: applied pulsed laser radiation (ω) *1*; sample *2*, photodetector *3*; the dashed line shows the second harmonic (2ω)

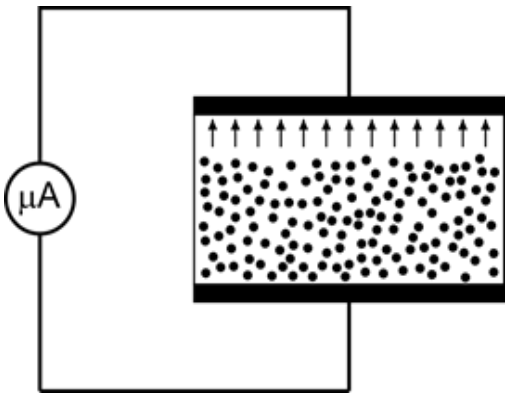

Fig. 4. Schematic for measurement of TSDC spectra of poled glasses; samples were subjected to linear heating, depolarization currents were measured with a microammeter(μA). Arrows show the direction of motion of mobile cations (see Fig. 1)

The scheme of TSDC spectra measurements is shown in Fig. 4. The spectra were measured under linear heating at a rate of 10°C/min; clamped graphite electrodes were used.

Experimental results

Fig. 5 (curve *1*) shows the dependence (on a logarithmic scale) of SHG signal intensity normalized to its maximum value, which has the form ln[$I(t)$/Imax], versus annealing time at 400 °C in poled glass. Apparently, the SHG signal relaxed almost completely in about 35 min and decreased to the level of the SHG signal generated by the non-poled glass surface.

The linear character of this dependence indicates that the SHG relaxation obeys the kinetics of the first order, and only one type of relaxant participates in the relaxation process.

The measurements of SHG signal relaxation kinetics carried out with a poled glass sample at a lower annealing temperature, namely, at 275°C, showed that in this case, the SHG relaxation kinetics is not described by a first-order reaction and the number of relaxors involved in the process is greater than one (see Fig. 5 (curve *2*)). Comparing SHG relaxation kinetics at temperatures of 275 and 400°C, we can conclude that during annealing at 275°C, in contrast to annealing at 400 °C, a process takes place in the glass that cannot be detected at 400°C because it proceeds too quickly at that temperature.

Fig. 6 shows the results of measuring the TSDC spectrum of poled glass annealed at 400°C for 50 min. It can be seen that a noticeable depolarization current appears only at temperatures above the glass transition temperature. The position of the first peak corresponds to 640°C. Since depolarization current is associated with movement of cations creating 'frozen' spatial charge, the peaks of TSDC spectrum should be related precisely to spatial charge relaxation.

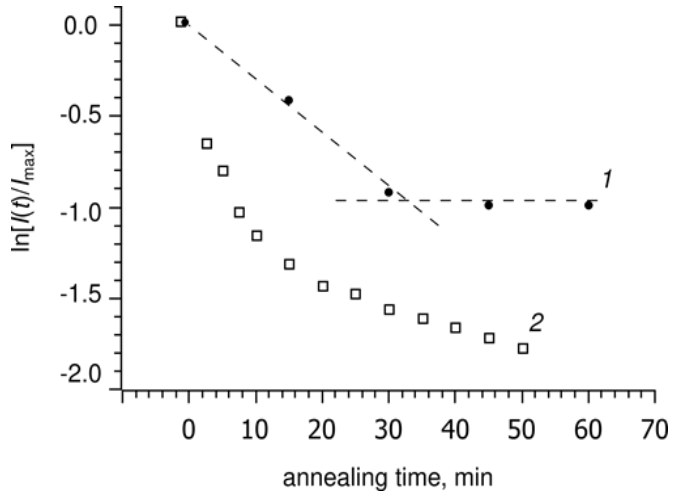

Fig. 5. Relaxation kinetics of normalized SHG at glass annealing temperatures of 400°C (*1*) and 275°C (*2*)

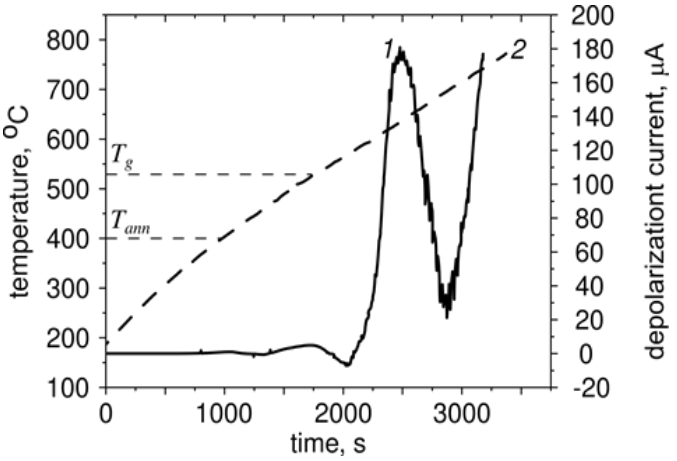

Fig. 6. TSDC spectrum (*1*) of poled glass after annealing at 400°C; the sloping dashed curve (*2*) corresponds to the temperature evolution (annealing and glass transition temperatures T_{ann} and *Tg* are shown by horizontal dashes)

Results and discussion

As mentioned in Introduction, the general consensus is that the appearance of SHG in poled glasses is due to the fact that charged particles (cations) shift towards the cathode during polarization, forming a spatial electric charge and a 'frozen' electric field. It is this field that disturbs the isotropic structure of glass, producing second-order optical nonlinearity. However, we found a high peak in the TSDC spectrum of poled glass that was subsequently annealed at 400°C, i.e., at a temperature much higher than the annealing temperature. This peak is observed at 640°C (see Fig. 6). Recall that the appearance of peaks in the TSDC spectra of poled glasses is related precisely to relaxation of the spatial charge. At the same time, 50-minute annealing of poled glass at 400°C leads to complete degradation of the SHG signal (see Fig. 5). This indicates that SHG in poled glass is not directly related to the spatial charge, since, according to TSDC data, the spatial charge relaxed at temperatures above 530°C (glass transition temperature), while the annealing temperature, which provides complete SHG relaxation, was only 400°C. It can be assumed that another mechanism is responsible for SHG, related to orientation of dipole structures formed by cations of alkaline (or alkaline-earth) elements associated with non-bridging oxygen atoms.

Conclusion

Thus, the experiments showed that 50-minute annealing of the given poled glass at 400°C leads to disappearance of second harmonic generation in the sample, with the characteristic relaxation time of about 30 min. Measurement of thermally stimulated depolarization current through this sample confirms the independence of the processes of relaxation of the spatial charge caused by glass polarization and relaxation of second harmonic generation. These relaxation processes occur at significantly different temperatures and, accordingly, are characterized by different relaxation times.

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