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EFFECT OF POLING CONDITIONS ON SECOND HARMONIC GENERATION IN FUSED SILICA

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Abstract

A systematic study of the effects of poling time and applied voltage on second harmonic generation (SHG) in thermally poled silica glass reveals that the SH signal is proportional to the square of the applied voltage, and that the speed of the poling process is inversely proportional to the applied voltage. Prior treatment of the samples is found to affect the poling process, and the optimum poling conditions are observed to depend on the poling atmosphere. The mechanism of thermal poling is discussed in the light of these new results.

In 1991 Myers et al [1] reported the observation a second-order nonlinearity of ~ 1 pm/V in thermally poled commercial fused silica. Their work has excited considerable interest because it offers the prospect of parametric frequency converters and linear electrooptic modulators monolithically integrated into optical fibres or planar glass waveguides. Since their original paper, thermal poling has been used to pole silica fibres [2] and to demonstrate linear electrooptic modulation [3-5] and quasi-phase-matched frequency doubling [6,7] of light. In some of these cases the vacuum poling technique [8] was used to improve reproducibility and quality of the induced nonlinearity. An effective second-order nonlinearity of ~ 0.2 pm/V [8] and an electrooptic coefficient of 0.05 pm/V [4,5] were obtained in poled silica fibres. The effective second-order nonlinearities were, however, still rather small. Considerable improvements may be expected by optimizing of poling conditions, e.g., the poling time and the applied dc field. Moreover, a better understanding of the mechanism of glass poling, which is still not fully understood, may help to improve the value of second-order nonlinearity in poled glass. Indeed, two mechanisms have been proposed to explain the thermal poling phenomenon. One is based on orientation of bonds or dipoles [9] and the other on a frozen-in electric space-charge field [10]. Despite of the fact that the frozen-in field is more likely to be responsible for the poling phenomenon, neither of these two mechanisms until now have obtained full confirmation. Both mechanisms predict the second-order nonlinearity to be proportional to the strength of the electrical field in the depletion region near the anodic surface ($\chi^{(2)} \propto V/d$, where V is the applied voltage and d the thickness of the poled region, i.e., the depletion region). Assuming that the pump propagates transverse to the poled region, the second-harmonic signal should therefore be proportional

to the square of applied voltage ($P_{2\omega} \propto (\chi^{(2)}d)^2 \propto V^2$). It has, however, been reported that the second harmonic signal is proportional to the third power of the applied voltage [1]. Both existing mechanisms of glass poling fail to explain this result. The dependence of the second-order nonlinearity on poling time (which may give important information about the poling mechanism) is also not fully investigated. Indeed, *in-situ* measurements of the second-harmonic signal during poling (with the applied voltage switched on continuously during poling) show a very rapid rise time of the second-harmonic signal over several seconds [9]. However, measurements of the second-harmonic signal *after* poling (no systematic measurements of such dependences have been carried out so far) show that it takes tens of minutes for the second-harmonic signal to saturate.

In this work, we carried out new experiments to clarify the influence of poling conditions, in particular the poling voltage and poling time, on SHG in thermally poled silica glass. We poled various types of commercial silica under the standard conditions: 280°C and 4 kV for 15 min. Table I shows the types of commercial silica used and their Na and OH contents, the existence of oxygen deficient centres (ODC) and result of SHG measurements. Typical sample sizes were 20 mm diameter and 1 mm thick. A Si anode and a stainless steel cathode were pressed to both sides of the samples. Q-switched (1 kHz repetition rate, 200 ns envelope duration) and mode-locked (76 MHZ repetition rate, 300 ps pulse duration) Nd:YAG laser pulses at 1064 nm were used as the pump source at an average power of 850 mW. Herasil 1 (Heraeus Silica & Metals Ltd) and OX (Nippon Quartz Glass Ltd) glass samples were prepared by flame fusion of quartz crystal powder. The UV silica we used was OX silica annealed in an oxygen atmosphere to improve the transmittance in the UV region. The values of Na content are quoted from the catalogues; it is difficult to clarify the effect

of Na content on SHG in these silica samples. OH content was determined from the absorption coefficient at ~ 2.73 μm with a molar extinction coefficient of 861 mol^{-1} cm^{-1} for OH.

Nasu et al reported that the SH signal is related directly to OH content for all the various silica samples prepared by different procedures [11], and a correlation between OH concentration and SH signal has been reported in fibre preforms [2]. In the present experiments we did not observe any clear relationship between SH signal and OH content in the silica samples.

The concentration of oxygen deficient centres (ODC's) was estimated by measurements of the absorption band at ~240 nm. UV silica without ODC's showed no SH signal, indicating that ODC's may be play a role in the formation of the second-order nonlinearity in fused silica. The concentration of the ODC's calculated from the absorption coefficient at 240 nm, using the Smakula's formula, is ~10^{16} cm^{-3} in our silica samples. This concentration is too small to explain the creation of the second-order nonlinearity by the orientation of oxygen deficient centres. Therefore the ODC must play a different role in the poling process, e.g., they may increase the mobility of cations in the glass.

We also examined the effect of poling conditions on SHG in fused silica samples poled both in air and an evacuated chamber. Figure 1 shows the SH signal versus poling time for samples poled in air (Fig.1 (a)) and in vacuum (Fig. 2 (b)). The samples were 3 mm thick, as received (new) Herasil 1 and were poled al 280°C. After poling for an appropriate time, samples were subsequently taken from the oven and cooled to room temperature. Vacuum

poling was carried out in an evacuated chamber at about 1.2×10^{-5} mbar. Since the cooling rate of the evacuated chamber was relatively slow (it took about 9 min for the temperature inside the chamber to fall from 280°C to 200°C), some poling is likely to occur even during the cooling stage of vacuum poling.

The experimental results show that the SH signal in air-poled samples increases exponentially with the poling time up to a saturation level. The growth rate clearly depends on the applied voltage. Indeed, the time $t_{1/2}$ taken for the amplitude of SH signal ($P_{2\omega}^{1/2}$) to reach its half-maximum ($P_{2\omega}^{1/2} = a(1 - e^{-t/\tau})$, where $t_{1/2} = \tau \ln 2$ and τ is the relaxation time) is 6.5 min, 7.8 min and 11 min for applied voltages respectively of 4 kV, 3 kV and 2 kV. This result gives approximately an inverse linear dependence of the time constant τ on the applied. Assuming that the poling phenomenon is caused by a frozen-in electrical field, the Maxwell relaxation time is $\tau = \epsilon\epsilon_0/\sigma$, where σ is the conductivity in the depletion region. The obtained linear dependence of the relaxation time on the applied voltage reveals that the conductivity inside the depletion region is linearly proportional to the applied voltage.

Results previously obtained by in-situ measurements of second harmonic signal (with applied voltage switched-on continuously), in particular the very fast rise-time (several seconds) and the independence of this rise-time on the applied voltage, seem to contradict the above results [9]. This contradiction may, however, be resolved as follows. It is necessary to suggest that the poling process in glass takes place in two stages. During the first stage, cations such as Na^+, H^+ or positive holes move to the cathode, leaving behind a negatively charged depletion region. During this stage a very high field arises in this region, between the negatively charged region and the anode. This field creates a second-order nonlinearity ($\chi^{(2)}$

$= 3\chi^{(3)} E$, where $\chi^{(3)}$ is the third-order susceptibility) and a corresponding SH signal which is detected during in-situ measurements. This nonlinearity contains no permanent contribution (it disappears after removal of the anode). The speed of the formation of the depletion region - several seconds - is determined by the cationic conductivity of the glass, which is relatively high at elevated temperature of about 280°C. Cationic conductivity takes place in the whole volume of the glass, where the strength of the electrical field is much lower than in the depletion region, which explains why this conductivity (rise-time) is independent of the applied voltage.

During the second stage of the poling process, separation of charges within the depletion region takes place under the action of a very high field. Electrons or negatively charged oxygen ions may be the charge carriers in the region. During this second part of the poling process, the frozen-in electrical field appears near the anodic surface, thus creating a permanent second-order nonlinearity. This process takes a much longer time (tens of minutes) because the mobility of the charge carries in the depletion region is very low. Conductivity in the depletion region will depend on the applied voltage due to the very high electric field strength (more than 10^7 V/cm) in this region. Indeed, the results of our experiment may be interpreted as an indication that the conductivity inside the depletion is inversely proportional to the electrical field strength (applied voltage).

Because of electrical breakdown, it was impossible to apply voltages higher than 4 kV to the silica samples in air. In vacuum poled samples, the SH signal shows a maximum for each dc voltage and this maximum shifts to a shorter poling time with increasing dc voltage applied. This result indicates that some species in the air, such as hydrogen or oxygen ions,

may be involved in the poling process. However, based on the current results it is difficult to give a more detailed explanation of the origin of this difference in the time dependences of vacuum and air poled samples.

Figure 2 shows log SH versus log dc voltage for as-received Herasil 1 samples. Samples were poled at 280°C for the optimum time needed to create the maximum SH signal for each dc voltage applied (see Figs. 1 (a) and (b)). Note that the line in this figure was fitted only to samples poled in air. The result of these measurements reveals that the SH signal is proportional to the square of the applied dc voltage, which agrees with the predictions of the depletion-region model in contrast with the cubic dependence reported in previous measurements [1]. Saturation of the SH signal is observed at dc voltages as high as 8 kV, in good agreement with the results of previous measurements [1].

To examine the annealing effect on SHG in fused silica, we used samples poled and annealed repeatedly. Sample annealing before poling was performed at 350°C for over 1 hour. Figure 3 shows the SH signal versus poling time at 280°C and 4 kV for Herasil 1 samples poled and annealed repeatedly. Already after 5 min of poling the SH signal is saturated in the annealed silica samples (in experiments with fresh as-received samples it takes an order of magnitude longer time for signal to saturate - Fig. 1). This indicates that annealing does not restore the initial properties of the silica sample, and that probably the conductivity in the region near the anodic surface irreversibly increases after the poling and annealing procedures. Figure 4 shows log SH versus log dc voltage dependence for repeatedly-poled and annealed Herasil 1 samples. All the samples were poled al 280°C for 15 min. The SH signal is clearly proportional to the square of the applied dc voltage without any sign of saturation as in the

similar dependence measured on the fresh samples.

In conclusion, we have demonstrated that the SH signal is proportional to the square of the applied dc voltage in thermally poled silica glass. This result is in good agreement with existing models of the poling phenomenon. It was found experimentally that the rise time of the SH signal is in inverse proportion to the applied voltage. This may be interpreted as evidence of the linear dependence of the conductivity inside the depletion region near the anodic surface on the applied voltage. A difference in the time dependence of the vacuum and air poled samples was observed. This may be interpreted as evidence that air species such as hydrogen or oxygen are taking part in the poling phenomenon.

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References

1. R. A. Myers, N. Mukherjee, and S. R. J. Brueck, Opt. Lett., **15**, 1733 (1991).
2. P. G. Kazansky, L. Dong, and P. St. J. Russell, Opt. Lett., **19**, 701 (1994).
3. X-C. Long, R. A. Myers, and S. R. J. Brueck, Opt. Lett., **19**, 1819 (1994).
4. A. C. Liu, M. J. F. Digonnet, and G. S. Kino, Opt. Lett., 1994, **19**, 466 (1994).
5. P. G. Kazansky, P. St. J. Russell, L. Dong, and C. N. Pannell, Electron. Lett., **31**, 62 (1995).
6. R. Kashyap, G. J. Veldhuis, D. C. Rogers, and P. F. McKee, Appl. Phys. Lett., **64**, 1332 (1994)
7. P. G. Kazansky, V. Pruneri, and P. St. J. Russell, Opt. Lett. **20**, 843 (1995).
8. P. G. Kazansky, L. Dong, ana P. St. J. Russell, Electron. Lett. **30**, 1345 (1994).
9. N. Mukherjee, R. A. Myers, and S. R. J. Brueck, J. Opt. Soc. Am. B **11**, 665 (1994).
10. P. G. Kazansky and P. St. J. Russell, Opt. Comm. **110**, 611 (1994).
11. H. Nasu, H. Okamoto, K. Kurachi, J. Matsuoka, K. Kamiya, A. Mito, and H. Hosono, J. Opt. Soc. Am. B. **12**, 644 (1995).

Figure captions

Figure 1 SH signal versus poling time in air (a) and vacuum (b). 3mm thick, as-received Herasil 1 samples. The lines show the guides to the eyes.

Figure 2 Log SH versus log dc voltage for as-received Herasil 1 samples. Samples were poled at 280°C. The poling time of the sample is an optimum one to show a maximum SH signal for each dc voltage. The line is fitted to samples poled in air. The slope of the line is 1.98.

Figure 3 SH signal versus poling time in air and vacuum for 1 mm thick, repeatedly-poled and annealed Herasil 1 samples poled at 280°C. The lines are guides to the eye.

Figure 4 log SHG versus log dc voltage for repeatedly-poled and annealed Herasil 1 samples annealed at 350°C for 1 hour before poling, and poled at 280°C for 15 min. The line is fitted to all the samples. The slope of the line is 1.92.