Appendix A: Thermal poling of glass: a brief introduction

Silica glass is an amorphous material and possesses inversion symmetry on a macroscopic scale. Hence the vanishing second order nonlinearity (SON), $\chi^2$, makes it impossible to use this material for efficient second-order nonlinear processes. Nevertheless, in 1980s many researchers reported on photoinduced second harmonic generation (SHG) from optical fibres by launching of strong Infrared (IR) beams from Nd:YAG lasers [1-5]. These were the very first demonstrations of breaking the symmetry of an amorphous material such as glass. Coherent photo-galvanic effect was identified as the cause of the photoinduced SHG, through which a spatially modulated static electric field along the fibre is established [6-10]. The electric field couples with third order nonlinearity (TON), $\chi^3$, of the glass and results in an effective $\chi^2$. The period of the self-organized electric field in the fibre alternates spatially to provide constructive interference through quasi-phase matching (QPM). The efficiency of the frequency doubling process was high enough to pump a dye laser with the green light produced by photoinduced SHG [3]. Following this demonstration a considerable research has been carried out in order to understand the fundamental physics behind the observed phenomenon and assess the compatibility of the new method with nonlinear crystals. Eventually, the efficiency of the photoinduced SHG was found to be limited by the low value of the nonlinearity, $10^{-3}$ pm/V, as well as by the length of the self-organized QPM-grating which cannot exceed 60-80 cm. (This was due to chromatic dispersion and phase modulation [4].) Efficiencies up to few percentages have been demonstrated [11-17], but unfortunately this figure did not make the photoinduced SHG attractive for real applications.

An important point in the search for an efficient glass-based second-order nonlinear material was the work of Myers et. al. in 1991 [18]. The authors observed that a permanent SON is induced in a fused-silica glass plate once heated to moderately elevated temperatures of 250°C-330°C with an applied voltage of about 3 kV -5 kV for 15 min with subsequent cooling to the ambient temperature with the voltage still applied. (This procedure is called the thermal poling of glass.) It has been suggested that a high electrostatic field $E_{dc}$, appearing in a thin depletion region near the anodic surface, is in fact responsible for the observed phenomenon, similarly to the explanation of the photoinduced SHG. Despite the vanishing $\chi^2$ in glass, the coupling between the electro-static field $E_{dc}$ and the intrinsic third-order nonlinearity of the glass resulted in observation of effective SON. According to Ref. [19] the SON and TON are related via the following equation:
This expression shows that the interaction between the TON and the electrostatic field produces the same effect as a SON on the optical field. For the strong field strength of $E_{dc} \sim 2 \times 10^9$ V/m [21, 22], fairly close to the dielectric breakdown of fused silica, and taking into account that for silica the $\chi^3$ is approximately equal to $2 \times 10^{-22}$ m$^2$/V$^2$ [20], the $\chi^2$ in poled glass is expected to be $\sim$1pm/V. This value was indeed measured experimentally and is of the same order of magnitude as the nonlinear susceptibilities of some of the widely used nonlinear crystals for frequency doubling, such as KDP ($\sim$1pm/V), BBO ($\sim$3.8pm/V), and quartz ($\sim$0.6pm/V) [23].

The mechanism that leads to the establishment of the SON in the glass has not yet fully understood. The origin of the electro-static field $E_{dc}$, responsible for $\chi^2$, has been subject of debate since 1990s, although poling had been studied before in the context of polymers [24, 25]. The application of high voltages to silica at elevated temperatures has been studied since 1970s, although not in the context of optics [26]. From these studies it was known that alkali ions such as Na$^+$ and Li$^+$, that are present in silica as impurities, are bonded to negatively charge non-bridging oxygen (NBO) sites, and may drift under the action of electric fields. It was also known, from the work of Myers’ and co-workers [18], that the nonlinearity was located in a thin layer, typically in less than 10 µm, beneath the surface of the glass plate that had been in contact with the anode electrode. As an explanation two mechanisms were proposed: either the nonlinearity was caused by orientation of bonds or by the creation of a space charge field, both leading to a DC electronic polarization [27, 28].

It has been suggested that the high temperature involved in the poling process increases the mobility of the impurities present in the glass, mainly alkali ions such as Na$^+$. Therefore, upon the application of an electric field, the positively charged sodium ions drift towards the cathode where they are neutralized by injected electrons. Under the hypothesis of zero ionic conductivity at the anode (blocking electrode), during the migration ions leave a negatively charged depleted region behind themselves. The depleted region is located a few microns beneath the anodic surface. Due to the lack of mobile charges the depleted region has a much larger resistivity than the rest of the glass. Like in a voltage divider, the applied voltage tends to mainly drop across the more resistive depleted region. As a consequence, a large static electric field is established between the depleted layer and the anode. The process is schematically represented in Fig. A-1.

Kazansky et al. distinguished between two possibilities that could arise at this stage [28]. In fact, either orientation of NBO bonds or glass ionization could take place under the action of the high electrostatic field. In the former hypothesis, the high temperature increases the mobility of the NBO dipoles, whereas the applied electric field forces them all to orient in the same direction. After cooling, the dipoles would be frozen in one direction, thus breaking the symmetry of the glass and accounting for the observed SON.

In the latter hypothesis, the static field is responsible for the ionization of the glass in the anodic region, leading to the creation of a positive charge layer that screens the external field and stops the process. When the sample is cooled down the ions are trapped in their positions. A high static electric field, between the positive layer and the negatively charged region, is then frozen in the glass once again breaking the centro-symmetric structure.
There are strong arguments against a significant contribution to the effective SON due to the orientation of dipoles in silica glass [29-33]. The theoretical models suggested for the poling process can be classified into two main groups, namely single carrier and multiple carrier models, namely single carrier model and multiple carrier model.

**Figure A-1:** A schematic representation of the thermal poling process.

As early as in 1953 researchers developed a model for the space charge build-up in alkali halide crystals [34]. The model can be easily adapted to the case of positive charge carriers. According to this model, Na\(^+\) is assumed to be the only mobile charge carrier. The anode is assumed to act as a blocking electrode, and under these circumstances electrical neutrality requires an equal amount of fixed negative charges to be present in the glass, for instance negatively charged NBO. (The NBO sites are assumed to be immobile.)

At steady state the electric field is given by [34]:

\[
E_{dc} = \frac{q_e N}{\varepsilon} (d_{dep} - x) \quad 0 < x < d_{dep},
\]

\[
E_{dc} = 0 \quad x > d_{dep},
\]

where \(d_{dep}\) is the thickness of the depleted region, \(q_e\) is the elementary charge, \(N\) is the fixed charge density associated with the NBO-hole centres and \(\varepsilon\) is the dielectric permittivity of glass. This simple model in fact is capable of describing all the essential features of thermal poling. During the migration of Na\(^+\), the charge front which separates the depletion region and the neutral region moves in the glass according to:

\[
d(t) = d_{dep} \tanh \left( \frac{t}{2\tau} \right),
\]

where \(d_{dep}\) and \(\tau\) in A.4 are given as following:
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\[ d_{dep} = \sqrt{\frac{2eV}{q_e N}}; \quad \tau = \frac{d_{dep}}{2\mu E_0}, \]

where \( \mu \) is the effective mobility of sodium. The motion of the charge front can be measured by the current that flows through the glass, taking into account that \( d_{dep} \) is much smaller than the thickness of the glass; the current can be well approximated by [34]:

\[ I(t) \approx I(0) / \cosh^2(t/2\tau), \quad (A.5) \]

Where the current at \( t=0 \) is given by: \( I(0) = [A q_e N d_{dep}/2\tau] \), where \( A \) is the cross section of the electrode.

Using the following known values for fused silica of [35]: \( \varepsilon = 3.8\varepsilon_0; N = 2 \times 10^{22} \text{m}^{-3}; \mu_{Na^+} = 1 \times 10^{-15} \text{m}^2\text{V}^{-1}\text{s}^{-1} \), the thickness of the depletion region can be calculated to be \( \sim 9 \mu\text{m} \). The depletion region for a 1mm thick silica glass is formed on the time scale of \( \sim 20 \text{ min} \) poled at 4 kV. This is ten times faster for a ten times thinner sample. The frozen electric field peaks at the surface in contact with the anode and its maximum value according to eq. A.2, is \( \sim 10^9 \text{ V/m} \) which is very close to the value of the electrical breakdown in silica. It suggests that high field ionization stops the poling process, as envisaged in [29]. As a consequence the SON is also limited in silica to values of \( \sim 1 \text{ pm/V} \). The applied field mainly alters the time scale of the process and \( E_{dc} \) depends on the charge carrier concentration. From this simple model it is possible to infer that a glass sample having lower charge concentration will exhibit lower nonlinearity and a wider depletion region. These results were confirmed by the findings of researchers reported in [36-39].

Although the single carrier model describes the general features of the poling process reasonably well, it did not account for some of the experimental evidence. For instance two time scales was found by researchers during poling and de-poling current measurements [35]. This behaviour was attributed to the presence of a second charge carrier with much lower, \( \sim \) an orders of magnitude lower, mobility. Indiffusion of H\(^+\) from the atmosphere, driven by the high electrostatic field, was thought to be taken place during the poling. Indeed the presence of a positive charge layer between the negatively charged depleted region and the anodic surface was revealed using a technique called “laser-induced pulse pressure (LIPP)” [31]. In [40] researchers pointed out the relevance of the poling atmosphere by performing poling in air or under vacuum (\( 10^{-8} \text{ atm.} \)). Samples poled in vacuum exhibit wider depletion regions and consequently lower nonlinearity compared to samples poled in air for the same time. It was speculated that H\(^+\)/H\(_2\)O\(^+\) may in-diffuse from the atmosphere, while poling in air [35, 40]. LIPP measurements also showed a different charge distribution for poling in vacuum and air. A positive charge layer was revealed to be present also in the samples poled in vacuum. It was therefore thought that, in vacuum, glass ionization with liberation of \( e^- \), must take place. The same phenomenon is probably occurring in air as well, but in that case in-diffusion of positive species from the atmosphere is believed to be the dominant mechanism.
Recently a study of the dynamics of thermal poling for different sample thicknesses was published, where researchers show the existence of an optimum poling time, ~10 min depending on the sample thickness, for which the achieved SON was maximized [41]. The decrease in SON for longer poling times cannot be explained by a single carrier model. In order to account for the new experimental findings new models have to be developed. In Ref. [35] two charge carriers with a very different mobility were considered. However, the same hypotheses as in Ref. [34] were used. Diffusion of ions has been considered by the authors in [42]. The models have shown good agreement with experimental results when applied to poling of a Suprasil silica glass. Other researchers have considered the ionization of the glass together with in-diffusion of H$_3$O$^+$ and H$^+$ from the atmosphere [43, 44]. The model predicts the existence of an ionosphere sandwiched between the positive charge layer and the negatively charged depletion region, in agreement with the findings of the researchers in [40].

Understanding of the physical mechanism behind the thermal poling is crucial for identification of the critical parameters affecting the process. Knowledge of this sort could lead towards engineering of the glass system and/or of the poling procedure for enhancing the induced second-order nonlinearity. However, much effort has still to be made towards the better understanding of the process. This can, for instance, be done by improving the characterization techniques and development of new methods for better accessing depletion region and obtaining information regarding its thickness, profile and dynamics.

References

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Appendix B: On the evolution of EFAD

This appendix is devoted to the importance of providing a good contact between the electrodes and samples and its role in evolution of the EFAD process. Essentially, in the context of the evolution of the EFAD process, the role of the glass-electrode contact can be considered if we recall that electrons tunnelling from ionised clusters have to be extracted at the anode. In order to gain a qualitative picture the following experiment was conducted. A 1mm thick polydisperse-type I-sample was equipped with two flat contact steel electrodes (6mm×9mm) so that the positive electrode was facing the nanoparticles containing layer. The sample was then placed inside the oven, and as explained in detail in 4.2, was subjected to the following treatment steps at ~280°C: 200 V -10 min (a), 200 V - 10 min (b); 200 V - 20 min (c); 200 V - 40 min (d); 400 V - 10 min (e); 600 V - 10 min (f) and 800 V - 10 min (h). Between each step of treatment, microscopic images of the sample were recorder. The results are shown in Fig. B-1.

As it can be seen, for treatment at 280°C, bleaching occurred with voltage as low as 0.2kV but did not cover the entire electrode area (Fig. B-1 a-d). Bleaching started in a central zone which covered approximately 13% of the total electrode area after 10min of treatment. It has to be pointed out that this zone was extended only slightly with increasing of the treatment time. After 10min treatment steps at 0.4kV (Fig. B-1 e) bleaching started near the electrode edges as well. However, it was only a treatment steps at 0.6kV and 0.8kV that the bleached zones in the middle and near the edges started to merge progressively (Fig. B-1 f and h, respectively). Finally, after 15min treatment step at 1kV, the entire area underneath the electrode was bleached (not shown here but for comparison see Fig. 4.7).

Mechanically contacted electrodes did not obviously provide a perfect uniform contact with the sample surface over the entire electrode area and the bleached zones were, hence, associated with tight contact. An evidence of this effect was found when the sample was probed in reflection from cathode side just after the poling step at 0.6kV while the anode stuck on glass surface due to electrostatic forces (Fig. B-1 g). Areas where tight contact was achieved were corresponded to bleached zones.

The present results show that physical contact (rather than ionised species from atmosphere [1]) is needed to extract electrons efficiently. The electrostatic force exerted on the sample is further enhanced due to ion migration during the treatment.

This can be qualitatively estimated as the electrostatic force between two plane electrodes is given by:

\[
F = 0.5\varepsilon_0\varepsilon_r^2S V^2 L^{-2},
\]

(B-1)
where \( S \) is the electrode surface, \( V \) is the applied voltage, \( L \) is the distance between electrodes and \( \varepsilon_r \) is the relative permittivity of glass sample sandwiched between the electrodes. When 1kV is applied to our sample at room temperature, the electrostatic force is as weak as \( F=1.2 \times 10^{-3} \text{N} \) (taking \( S=54 \text{mm}^2, L=1 \text{mm} \) and \( \varepsilon_r=2.2 \)). At elevated temperatures, however, the applied voltage drops almost entirely across the ion-depleted layer [1]. This results in much stronger electrostatic force due to the decrease of the effective distance between the electrodes.

An important point to consider is that for the experiments presented in the main body of the thesis flat press contact steel electrodes were used. While these electrodes considerably improve the homogeneity of the contact between the electrode and glass, but the overall contact is still far from perfect, as some jumps in the current evolutions were indicated (See for examples Fig. 4.12). The contact can be further improved by using a carbon ink layer between the electrodes and glass. However for the experiments described in the thesis this technique was not applied.

**Reference**