Poled glasses and poled fibre devices

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This paper reviews the field of poled glass and poled fibre devices with a specific focus on silicate glasses and fibres. The technology is presented along with detailed discussion of the mechanism involving charge separation and trapping. The potential role of field induced crystallisation is discussed and several emerging applications are presented.

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1. Introduction

1.1 Overview

Silica glass is technologically very important, especially in telecommunications, because of its excellent properties such as strength and the ability to draw into fibre and optical properties including very low loss. An important and interesting optical property is non-linearity. Silica glass exhibits very low non-linearity and hence has almost no role in the active routing or processing of information.

Poling is a technique that permits the modification of silica glass to enhance the non-linear properties. Over the last ~20 years, several research groups have been developing this technique, revealing much interesting materials science and scope for further improvement in the non-linearity.

This review paper starts by describing the basics of the poling technique; especially the most commonly used “thermal poling” technique. A review of the mechanism involved in poling, and the techniques used to reveal it, is presented. The role of different glass compositions is then explored. Various other poling techniques and their effects are presented, leading into a discussion of structural modification of the glass; an exciting area where much further work remains to be done. The paper concludes with a discussion of the applications of poled silica fibre.

1.2 Optical nonlinearities

Optical non-linearity is generally described in terms of a polynomial expansion of the susceptibility, \( \chi \); a complex quantity with the real part describing the delay and the imaginary part the loss (or gain) experienced by propagating light. The real part is directly related to the refractive index of the material. The polarisation, \( P \), in terms of an expansion of the susceptibility and electric field, \( E \), is as follows:

\[
P(\omega) = \varepsilon_0 (\chi^{(1)} E + \chi^{(2)} E^2 + \chi^{(3)} E^3 + ...) \tag{1}
\]

where \( \varepsilon_0 \) is the vacuum permittivity. \( \chi^{(1)} \) is directly related to the refractive index, \( n \), \( \chi^{(2)} \), is of most significance to poling; it describes how the refractive index varies linearly with applied field, \( \chi^{(3)} \) to give rise to the Third Order Nonlinearity (TON) or the non-linear optical non-linearity which describes how the refractive index varies with the square of field, or optical power. In silica glass the TON is very small, typically \( \approx 2 \times 10^{-22} \text{ m}^2/\text{V}^2 \).

The centrosymmetry of silica glass means that the \( \chi^{(2)} \) is zero. Poling is the process that induces a non-zero \( \chi^{(2)} \). \( \chi^{(2)} \) gives rise to the Second Order Nonlinearity (SON) and the Linear Electro-Optic (LEO) coefficient. The LEO coefficient, \( d \), linearly related to \( \chi^{(2)} \), is used to describe the interaction between an optical frequency wave and a low frequency (or DC) applied field. The SON coefficient, \( d \), linearly related to \( \chi^{(2)} \), is used to describe the interaction between two optical frequency waves. For silica \( r \) and \( d \) have similar values. These coefficients (and \( \chi \)) are tensor quantities as their magnitudes depend on the relative polarisations of the fields involved. When used without the tensor subscripts the maximum value is implied; for \( d \) this would be \( d_{33} \), where the polarisation of the incident field is along the poling direction. \( d_{13} \) is where the polarisation of the incident field is normal to the poling direction. A ratio of 3:1 is normal between these two components. For electro-optic modulators a Figure of Merit, \( V_g L \), inversely proportional to \( r \), is used.

1.3 Basic mechanism

The poling process modifies the glass to break the inversion symmetry and create a non-zero SON (or LEO). There are essentially two different ways for this to happen: molecular alignment or charge separation.\(^{1,2}\) As will be discussed later, the experimental evidence strongly supports the latter in the overwhelming majority of cases. This involves the migration, and subsequent freezing-in, of charges creating a space charge field within the material. This internal field then acts on the \( \chi^{(1)} \) to give a \( \chi^{(2)} \).

\[
\chi^{(2)} = 3 \chi^{(3)} E_{id} \tag{3}
\]

A simplified description of the space charge field mechanism is as follows:

- The glass contains many charges (e.g. alkali ions) which at room temperature are immobile and generally located near defects in the glass matrix that can provide a matching charge.
- On heating to a certain temperature these charges become mobile and can move through the glass.
When a strong electric field is also applied these charges migrate to the electrode of opposite charge.

If the sample is allowed to cool whilst the electric field remains applied, the charges will become immobile again. This freezes into the glass a space charge field.

This internal field acts on the TON to create a SON.

As will be discussed later, the actual mechanism appears to be rather more complex than this.

1.4 Poling techniques

In 1986, Österburg and Margulis unexpectedly discovered that SHG could occur in a silicate optical fibre simply as a result of it guiding strong (~100 GW/cm²) laser light. The SHG efficiency was as high as 5% in fibres less than a metre long; but took many hours to build up. In 1987, Stolen and Tom reduced this time to minutes by seeding with the SH wavelength. They proposed that intense fields at the pump and SH wavelengths mixed to orient defects inducing a χ(2) with the correct spatial period for efficient SHG.

Poling with an intense internal field led to investigation of a strong external electric field. In 1989, Li and Payne performed the first demonstration of poling in fibre. They used, at room temperature, a twin hole fibre with internal electrodes, producing an electro-optic coefficient of ~10⁻⁴ pm/V.

Subsequent research performed at elevated temperature induced larger electro-optic coefficients. Myers et al. advanced poling of bulk silica; in 1994 they induced a LEO of 0.3 pm/V in silica. In 1994, Digonnet et al. demonstrated similar results for a silica channel waveguide. In 1994, Kazansky et al. externally poled a side-polished optical fibre achieving 0.2 pm/V. Then in 1995, Fujiwara et al. poled a special optical fibre with internal electrodes achieving electro-optic values in the region of 1 pm/V.

The use of lasers as the stimulus for poling has been explored; using infra red CO₂ lasers and ultraviolet lasers. The CO₂ laser is essentially a precise, localised and rapid heat source. This technique, reported in 2001 by Blazkiewicz et al., produced similar results to regular thermal poling (see Section 4.1). The UV technique, reported in 2001 by Blazkiewicz et al., produced similar results to regular thermal poling (see Section 4.1).

Other techniques include corona poling of glass films, e-beam poling of lead silicate glass, and proton implantation using a pelletron.

1.5 Poling technology

Various different approaches to poling have been taken. As well as the use of different stimuli, as discussed in the previous section, different types of sample, such as planar, both uniform and with waveguides, and fibre, have been used. Our research has focussed on thermal poling of fibre and uniform planar samples.

Fibres used in poling are generally fabricated by the Modified Chemical Vapour Deposition (MCVD) method with Ge-doped cores. There are two types: twin-hole fibre and D-fibre. Twin-hole fibre has two small holes in the cladding that run close and parallel to the core. Electrodes are inserted into these holes, both for applying the poling field and for subsequent EO modulation (see Fig. 1). D-shaped fibre with a single hole has one internal, inserted wire, electrode and one external electrode placed against the flat of the D.

Typically the core is closer to one electrode than the other since the SON was typically to be located a few microns under the anode (“the anode effect”) as this is where the deple-
space Mach Zehnder Interferometer. A complex arrangement of modulation on both arms and quadrature detection permits accurate measurements in a rather unstable environment over long times. The system permits the EO coefficient to be continuously monitored whilst poling. The measured response in a waveguide involves an overlap integral between the propagating mode and the local distribution of EO coefficient.

The time evolution of the EO coefficient in a poled fibre was measured. The fibre was poled at 3.5 kV and 280°C for 4000 s. The evolution (Fig. 2) goes through several phases.

The initial (t = 0 s) value of ~0.06 pm/V simply arises through the external applied field acting on the \( \chi^{(3)} \) to give a \( \chi^{(2)} \). No poling has occurred at this time.

Between 0 s < t < ~100 s, the EO coefficient rapidly drops as a shielding field is established due to the relatively rapid migration of the mobile charges; understood to be Na⁺. This results in a build up of Na⁺ in the vicinity of the cathode and a depletion region in the vicinity of the anode where there is an excess of the immobile negative charges that had previously been the sites of the mobile Na⁺.

This depletion region gives rise to a strong negative charge, and hence electric field, in the material in close proximity to the anode. This is at a maximum at the surface (Section 2.3) and locally this field can be several orders of magnitude greater than the applied field. This intense field causes the migration of a second species in from the surface of the glass. This species has not yet been positively identified but is widely accepted as being a hydrogen species, most likely either H⁺ or H₂O⁺ and is much less mobile than Na⁺. As it moves into the glass it modifies the local field distribution. The field set up between this migrating front of H⁺ ions and the depletion region acts on the \( \chi^{(3)} \) to give a \( \chi^{(2)} \). As this front moves towards and across the fibre core (~100 s < t < 4000 s), the measured \( \chi^{(2)} \) reaches a maximum value (of ~0.12 pm/V after ~3000 s in the results shown).

During poling, in general, two fields are acting on the glass: the applied field and the field resulting from migration of charges. When the poling field (and the heat) is removed, the observed EO coefficient drops, but the field arising from the non-uniform distribution of charges remains. As the heat has been removed, these charges are rendered immobile so this field is “frozen in”. This field gives rise to the residual, induced \( \chi^{(2)} \) of ~0.06 pm/V observed at 4000 s and is nominally permanent. This is the poled \( \chi^{(2)} \).

2.2 Optimisation

Equation 3 appears to place an upper bound on the achievable \( \chi^{(2)} \) if the frozen-in field cannot exceed the breakdown strength of the glass. For silica this and the \( \chi^{(3)} \) value are known, ~10⁹ V/m and ~2 × 10⁻²² m²/V² respectively, and thus a maximum \( \chi^{(2)} \) would appear to be ~0.6 pm/V.

Substantial research has been performed to maximise the achievable \( \chi^{(2)} \). Two parameters that are readily variable are the applied voltage and the poling temperature. Several researchers have investigated the role of these parameters in poling for different materials and setups. They all reach broadly similar conclusions.

In 2005, Lee performed an extensive and systematic study using different voltages and temperatures (200°C, 250°C, 280°C and 300°C, and 1 kV, 2 kV and 3.5 kV), keeping other parameters fixed. Figure 3 shows comparisons; the shapes are very similar although the scaling differs with conditions. At 200°C (Fig. 3a), the evolution is slow and the initial dip can be seen. It is apparent that the speed of migration of the charges responsible

Fig. 2. EO coefficient time evolution in thermal poling.

Fig. 3. Comparison of EO evolution for different poling conditions (From Ref. 21).
for establishing this feature is strongly dependent on the poling voltage. At 3.5 kV this is a transient feature on the axis, whereas at 2 kV it evolves over many hours. At the higher temperature of 250°C (Fig. 3b), this transient is barely visible at either voltage on the scales shown. However the subsequent rise due to the injected species is now clear and occurs much faster for the higher voltage. At the even higher temperature of 300°C (Fig. 3c) the EO coefficient has passed the peak in this time period. Interestingly, whilst for the higher voltage the rise is much faster, it reaches its peak value some time after the lower temperature case. The higher voltage poling also reaches a higher value of induced EO coefficient.

Lee’s results provided substantial evidence for the trends observed by others. Two key conclusions are that the induced EO coefficient increases with increasing voltage and it initially increases with temperature up to a saturation value. This is in agreement with the model as lower temperature results in lower charge mobility and lower voltage results in a lower force to move the charges. For this type of fibre, approximately the same EO coefficient can be achieved for temperatures in the range 250°C to 300°C, simply by poling for different times.

Other results have suggested a quadratic dependence of induced EO on applied voltage. Note of course that there are limits to the voltage that may be applied: as well as surface tracking or immediate dielectric breakdown, effects of charge migration cause eventual breakdown for prolonged poling at high voltage.

2.3 Modeling

In 1987 Stolen and Tom explained the self-induced SHG as the incident light at \( \frac{\chi}{\chi^2} \) to generate a DC polarization field, which then orients defects to induce a macroscopic \( \chi^2 \) with the correct spatial period to generate efficient SHG. Kazansky and Russell, in 1994, first proposed that the effect was due to an internal space charge field caused by charge migration acting on the \( \chi^3 \) to give a \( \chi^5 \). Supporting evidence for this model came from secondary ion mass spectroscopy and laser induced pressure pulse probe. Alley et al. in 1998 extended this model suggesting a second species \( \chi^5 \) (e.g. \( \frac{\chi}{\chi^2} \)) is injected into the glass from the anode surface.

Based on earlier charge separation models, Quiquampois et al. produced a detailed theoretical analysis. It assumes a single ionic charge carrier that is initially bound to immobile charges and models the migration of mobile charges and the resultant internal field distribution on application of a voltage. The model includes charge dissociation and recombination effects. It produces a number of important conclusions:

i) There is a threshold, \( V_t \), for the applied voltage, \( V_{\text{app}} \) below which poling does not occur. For these lower voltages, charge recombination dominates over conduction or charge migration.

ii) For \( V_{\text{app}} < V_t \), the internal field in the glass is uniform and, after poling has finished, zero.

iii) For \( V_{\text{app}} > V_t \), there are three regions within the glass:
   a. A narrow layer close to the anode, depleted of mobile cations, which thus has a strong internal field, and hence should have a strong SON.
   b. A much narrower layer close to the cathode, with an excess of mobile cations.
   c. A region in between with uniform low internal field (determined by \( V_t \) not \( V_{\text{app}} \), which on the removal of the applied field becomes negligible and hence has no SON.

iv) The width, \( x_s \), of the anode layer is determined by \( V_{\text{app}} \) and \( V_t \), which is largely determined by the charge density. The field distribution within this region is linear and the maximum field at the surface can be several orders of magnitude greater than the applied electric field.

v) The electric field distribution is determined by the applied voltage, not the applied electric field.

When considering experimental results it is important to understand the assumptions of this model. Firstly, \( x_s \) is much smaller than the total thickness; which is generally true for planar glass samples (\( \text{nm} \)), but not for fibre (\( \text{mm} \)). Secondly, the electrodes are “blocking”; that is no charged species can exit, or enter the glass. The latter is actually invalid for most of the practical situations. \( \text{Na}^+ \) is known to exit from the cathode face. More importantly; injection of a hydrogen species from the anode surface is a critical part of the poling mechanism. However the model is very valuable, especially as the timescales for \( \text{Na}^+ \) migration and \( \text{H}^+ \) injection and migration are very different.

Efforts have been made to extend the modelling to two species. Kudlinski et al. included \( \text{H}^+ \) for thick Infrasil samples. Lee applied this model to twin hole fibre and the two species \( \text{Na}^+ \) and \( \text{H}^+ \). A particular problem was how to handle the hydrogen injection. Lee used a constant initial injection rate when hydrogen ions were plentiful, then as ions depleted, he used a rate proportional to these remaining ions.

2.4 HF etching

A frequently used method for investigating the location of the SON is etching the thermally poled silica plates or optical fibre with hydrofluoric acid (HF). There are two distinct ways in which HF etching has been used. Firstly it has been used to reveal the spatial distribution of the depletion region or charges in a poled fibre cross-section, since HF preferentially attacks the regions with strong electric field or charges. Secondly it has been used to measure the depth of the depletion in bulk samples by gradually removing material from the anode surface.

In 1999 Wong et al. used HF etching to reveal an etched ring around one electrode hole of a poled twin hole fibre. It was postulated, and is generally accepted, that this ring indicated the location of the charges or the position of the internal electric field between two regions of charge. The distance of this etched ring from the anode was found to increase with poling duration. Similar work by Myrén et al. in 2004 revealed a wide wedge-shaped depletion region. The fibre had smaller, and relatively more widely separated, electrode holes with Au–Sn alloy electrodes drawn into the holes as a liquid at 300°C. This technique was also used to study the time evolution (see Section 2.7).

Several researchers have used HF etching to determine the depth of the depletion region. In 1996 Margulis and Laurell used an interferometric setup to monitor the etching progress. Subsequently, in 2003, Triques et al. characterised the time evolution of the depletion region. Also in 2003, Kudlinski et al. applied a layer peeling technique to HF measurements that were interferometrically monitored to achieve sub-micron resolution characterisation of the spatial distribution of the non-linear region. These studies provided strong support for the charge migration models that were being developed at this time.

However the drawback to this HF etching method is that it cannot distinguish between contributions to the HF etching rate change from changes of electric field and charge densities, which are both present in the SON layer. Also, the etching rate is altered not only by the presence of electric field in the SON layer but also by the Ge doping in the fibre core and the stress at the core-
cladding interface due to the difference in fibre core and cladding materials.

2.5 SH microscopy

An important advance in being able to ascertain the location and movement of the SON during poling was the application of Second Harmonic (SH) microscopy by An et al, producing regular and SH images that could be overlaid. Samples (affixed to a substrate) were cut parallel to the direction of the applied electric field to expose the cross section. The surface of the cut sample was further polished to optical finish.

A typical result for a plain sample of fused silica poled at 3.5 kV and 280°C for 30 min is shown in Fig. 4. Figure 4a is an image of the area where the SH microscopy was performed. The interface between the anode surface and substrate can be clearly seen. The SH signal (Fig. 4b) reveals a bright narrow line just under the anode surface, corresponding to a well-defined SON spatial distribution. Some discontinuity along the line can be observed, believed to be mainly due to the inhomogeneities in the fused silica. An overlay image is shown in Fig. 4c.

The SON distribution can be calculated from the square root of the SH intensity to give a line scan across the SON layer (Fig. 5). The peak is ~5 μm under the anode surface and is ~7 μm wide. By reference to a quartz plate, the $d_{33}$ is 0.3–0.5 pm/V. The SON profile is asymmetrical, increasing relatively sharply at the side closer to the anode, reaching the maximum value and then tailing away deeper into the sample, as is expected. This analysis was repeated for samples poled for different durations. With increasing poling time, the SON layer moves deeper into the material (Fig. 6), consistent with the model of H+ moving in from the anode.

This measurement technique was extended to optical fibre, initially a single hole D-fibre, which was poled under typical conditions. Figure 7a shows the fibre geometry (the potting epoxy appears brightest in the image). Figure 7b shows the SH image: the SON appears around the anode in a thin layer. The depth and $d_{33}$ were similar to those in the planar fused silica sample, although the width is ~3.4 μm (a good match to the core size in these fibres).

The measurement was repeated many times and the SH signal invariably appeared as a more or less complete ring around the anode hole, indicating the charge distributes over the glass surface. (Also clear in Fig. 8, where the SON migrates in from the entire external surface). The incompleteness has two components. One of these is due to the polarisation sensitivity of the measurement. The other, which was randomly oriented, is likely due to the random position of the closest point of the 50 μm electrode wire to the edge of the 75 μm hole.

2.6 Interface effects

Figure 8 displays some interesting features in the vicinity of the core. The otherwise uniform SON layer is significantly perturbed in this region.

An and Fleming investigated this using D-fibre poled with var-
ious conditions.\textsuperscript{36,37}) Figure 9 shows the SON layer revealed by SH microscopy for two samples of fibre poled with typical conditions of 280° C for 30 min. The fibre in Fig. 9a was poled at 2 kV. The SON is largely a straight line except in the vicinity of the core where it appears to be held back somewhat. This result was initially rather surprising. Whilst charge mobility in germanosilicate glass depends generally in a non-monotonic manner on Ge concentration, for the concentration (~4%) in the core of these fibres, the charge mobility should be greater than in silica.\textsuperscript{38}) However the mismatch between the two glasses at the interface between the core and the cladding glass has numerous defects and frozen-in stress which presumably acts as a barrier.

To assess the possibilities for overcoming this barrier effect consideration of the ion mobility reveals two main factors;\textsuperscript{38) temperature and applied voltage. Increasing the temperature increases the mobility. Application of the poling voltage will linearly decrease the activation energy in the poling direction.\textsuperscript{36)} Thus higher poling voltage should result in greater charge mobility (in the poling direction). These two possibilities for overcoming the impeding effect of the interface were investigated.

Figure 9b shows a fibre poled under the same conditions but with the poling voltage raised from 2 kV to 3.5 kV. There are several interesting features. Firstly, and as expected, in the cladding the SON layer has penetrated further due to higher mobility. In the vicinity of the core, the SON layer is mostly still held back by the interface. However, importantly, the increased mobility has permitted the SON to penetrate the core-cladding barrier. Furthermore, where it has moved into the core, it has then moved
much faster than in the cladding. This is consistent with the expectation of greater charge mobility in the germanosilicate glass. Higher voltages and longer poling times increased this effect.

Figure 9c shows a fibre poled under similar conditions to that in Fig. 9a however this time the temperature has been increased to 320°C. The ion mobility is much higher in this case, and the SON layer has clearly passed through the whole core region. The impeding effect of the core-cladding interface is still visible from the fact near the interface there is a perturbation to the SON layer; specifically it lags behind here somewhat.

2.7 Time evolution

A more direct technique than interferometry (Section 2.1) for measuring time evolution uses HF etching (Section 2.4). In 1999, Wong et al. made HF etching measurements on two samples of a fibre poled for different durations and found that the ring around the anode moved deeper into the fibre with longer poling time.30) In 2005, Myrén et al. applied this technique to a twin hole fibre that was poled with a temperature gradient along its length, to approximate different poling durations.39) This provided a sequence of cross-sectional views showing the progress of the etched layer through the core, supporting their analysis that the internal field should reverse direction as this layer moved through the core. However, HF etching is again an indirect measurement since the etching rate is not directly connected to the non-linearity.

In 2006, An and Fleming applied SH microscopy to multiple samples of the same fibre poled for different durations, to study the evolution of the SON layer.40) The fibre was a standard poling D fibre and was poled for 2, 5, 10, 20, 30, 45, and 60 min. Overlay micrographs from the polished ends of the fibres are shown in Fig. 10 (the flat is vertical and on the left). The SH active region was confined to a narrow layer:

- After 2 min, the SON layer was already very strong and was parallel to the anode flat except at the core-cladding interface, where a hindering effect on the SON evolution was evident (Section 2.6). The core was already partly SH active with a larger SON than in the cladding, indicating that charges had partially overcome the barrier this interface presents.
- After 5 min, the SON layer had moved further into the fibre, but was still hindered partially at the core-cladding interface.
- After 10 min, the SON layer moved further into both the core and cladding and almost the whole fibre core became SH active.
- After 20 min, the SON layer fully overcame the core-cladding interface and reached the centerline between the two electrodes. The slight bulge on the SON layer behind the fibre core suggests higher ion mobility in the Ge-doped core than in the pure silica cladding.
- After 30 min, the SON layer was closer to the cathode than the anode. The SON layer has distorted; its wings are further away from the anode, probably due to the local direction of the electric field.

![Fig. 10. SH overlay micrographs of SON spatial distribution in fibre samples thermally poled at –3.5 kV and 320°C for different durations.](image)

![Fig. 11. Time evolution of the position and magnitude of the SON layer. (a) Evolution of SON layer position (The straight line is provided solely as an aid for visualization and not a fit or theoretical value). (b) Evolution of nonlinear coefficient magnitude.](image)
• At 45 min, the SON layer reached the edge of the cathode and was blocked. It further distorted, with the wings, unhindered by the hole edge, moving further away from the anode surface.
• After 60 min, the SON layer was still blocked at the edge of the cathode and the SH was much weaker.

The centre position and magnitude of the SON layer was measured for each poling duration and its evolution is shown in Fig. 11. The SON layer moved essentially linearly towards the cathode with poling time (Fig. 11a). The magnitude of the SON (Fig. 11b) first increased with time, reached a maximum $d_3$ value of ~0.32 pm/V between 5 and 20 min, and then decreased for longer poling time. At 30 mins, the SON was large ($d_3 = 0.26$ pm/V) even though the SON layer had passed through the core. Thus it is clear that poling fibre does not need the core in the close vicinity of the anode hole, making it easier to fabricate. Fibre with a central core was made and poled and SH microscopy revealed a strong SON in the core.41

3. Analysis of different glasses

The discussion so far has related to how the poling conditions can be varied and the impact that this has on the induced non-linearity. The other parameter that can be controlled is the material. There are several different aspects to this. Firstly, the dominant mechanism is the migration of charges. Thus the concentration of charges and their mobility in the glass are important and these can both be affected strongly by the material used. Secondly, the induced space charge field acts on the TON to produce the SON. Thus a material with a substantially larger TON would be a good candidate for producing higher SON. Thirdly, an important practical concern is the lifetime of these thermally induced effects. A material with lower mobility at room temperature would increase lifetime.

3.1 Poling various glasses

Whilst this paper is concerned with silicate glasses it is important to note that poling has been performed on various other glasses, including tellurite,42 chalcogenide,43 silicon oxynitride,13 and on other materials including polymers and of course non-linear crystals such as LiNbO3. This section considers the poling of several different bulk silicate glasses.

3.1.1 Borosilicate

The stability or lifetime of the induced SON is a very important practical consideration. It is directly related to the space-charge recombination process, which is governed by charge diffusion and field-driven migration in the poled glasses. From the viewpoint of charge mobility, a glass material with higher activation energy for the migrating charge that is responsible for the annihilation of the space-charge field would be preferable. Borosilicate glasses seem to fulfill this requirement and have been demonstrated to slow down charge migration and significantly enhance the SON stability in thermally poled bulk samples.44

In 2006, An and Fleming used SH microscopy to characterise thermally poled, commercially available, borosilicate glass (0.15-mm-thick Schott D263 microscope cover slips, with compositions by weight of 64.5% SiO$_2$, 6.4% Na$_2$O, 6.9% K$_2$O, 7.7% B$_2$O$_3$, 4.5% Al$_2$O$_3$, 5.9% ZnO, and 4.1% TiO$_2$). The samples were poled at 300°C and, due to higher conductivity, at a lower voltage (1–2 kV) which had to be applied gradually.

A SON layer was found in all samples poled above 1 kV (again showing a voltage threshold) and scaled with poling voltage: the magnitude of the induced SON, $d_3$, was measured to be 0.18 pm/V for the 1.4 kV poled sample and 0.22 pm/V for the 1.8 kV poled sample. For the sample poled at 1.8 kV the SON layer was found to be only ~0.8 μm under the anode surface.

SEM and EDS analysis were performed on the poled samples and substantial compositional and structural changes were found in the near-anode region of the poled glass. K$^+$ ions had migrated entirely out of a region ~3 μm below the anode and then had built up a K$^+$ enriched region in the next ~1 μm. Considering relative mobilities, it was assumed that Na$^+$ ions had migrated entirely out of this region. Interestingly, and consistent with the model of the injection of a hydrogen species, the SON layer is entirely contained within this alkali ion depleted region. On the cathode surface, several crystalline phases formed (white dendrite precipitates) as a result of Na$^+$ ions being reduced at the cathode surface, providing strong evidence that the Na$^+$ ions not only migrate entirely to the cathode but can be removed from the glass (inconsistent with the “blocking electrode” assumption generally used in modeling).

3.1.2 Soda lime

Soda lime silicate (SLS) glasses are attractive for optical devices since they are less expensive than fused silica but still possess excellent optical transparency and good chemical and mechanical durability. Margulis et al have poled these glasses, both to create SON46 or fabricate planar waveguides47 through the field-driven migration of cations.

An and Fleming poled commercially available 1 mm SLS glass samples,48 at either 230°C or 280°C at 1.0–2.0 kV; again gradually to avoid problems due to higher conductivity. SH microscopy again revealed a SON layer beneath the anode, its intensity being lower than, but still comparable to, those observed in thermally poled fused silica glasses. The layer was ~1.5 μm beneath the anode surface which is smaller than that for fused silica. This difference can be attributed to the relatively high concentration of alkali ions in SLS glasses. In both fused silica and soda lime glass, Na$^+$ is the most mobile ion that plays a dominant role in the creation of a cation-depleted region. It is also known that the SON layer is formed within the depletion region. In SLS glasses, the number density of Na$^+$ ions is much higher than that in fused silica, resulting in a narrower depletion region and a SON layer much closer to the anode surface.

As well as demonstrating that the mechanism is essentially similar and that these technologically important glasses can be poled, the research revealed significant structural changes. On the cathode surface white precipitate appeared and by XRD the main crystalline phase was determined to be sodium metasilicate, Na$_2$O·SiO$_2$·nH$_2$O, indicating that Na$^+$ ions exited the cathode surface. Also a layer of pillar-like features perpendicular to the surface was seen under the anode and attributed to field-driven phase separation.

3.2 Glasses with regions of different composition

The above discussion suggests that the performance of devices could be tailored by structuring the glasses with regions of different compositions. It is important to consider the impact of interfaces on ion migration. One critical practical performance issue is the lifetime of these thermally induced effects. The impeding effects of interfaces might be used to stabilise the non-linearity.

Borosilicate glass can be made by MCVD and can be poled and since it has a higher activation energy it is a good candidate for stabilising the SON.44 Xu et al studied a fibre where a layer of borosilicate glass had been deposited within one of the electrode holes.49 Isochronal annealing studies showed (Fig. 12) that...
there were two components to the decay: a fast initial decay followed by a slower long-term decay. The borosilicate ring served to reduce the amount of the initial decay and the slope of the long-term decay. The overall lifetime enhancement was a factor of four.

In 2005, An and Fleming used SH microscopy to examine the SON profile in such a twin-hole fibre, thermally poled at different voltages. At lower voltages (< 3 kV), the induced SON layers were totally confined within the borosilicate layer. However at higher voltages, even up to 4 kV, the SON layer was still tightly confined within the 2 μm-thick borosilicate layer around the anode hole except at the core-cladding interface where the SON had overcome the borosilicate layer and penetrated into the fibre core.

The confinement of the SON layer to the borosilicate region is consistent with the reduced mobility of Na⁺, and particularly H⁺, in this glass. The penetration into the core probably results from the core region being in contact with, or even slightly extending into, the borosilicate layer and the H⁺ ions having substantially higher mobility in the germanosilicate core glass. They then appear to have been hindered at the far core-cladding interface, either due to the lower mobility in the silica cladding, or possible interface effects. A line-scan revealed that the SON profile in the fibre core is much wider and flatter than that in a standard poling fibre; indeed it appears to completely fill the core. This result is significant, considering the overlap between the SON and the fibre guided modal field.

Similar work was performed on fibre with an Er-doped germanosilicate ring around the anode hole by Blazkiewicz et al. This showed a more rapid saturation of the induced LEO value.

In 2006, using fibre drawn from the same preform, An and Fleming characterised the SON distribution with SH microscopy. The fibres were poled at 280°C for 30–120 min with voltages 3.0–4.5 kV applied and then measured with the SH microscope. Again it was found that the ring around the anode hole effectively trapped the non-linearity. This time, for poling voltages greater than 4.0 kV and poling times shorter than 60 min, the SON layer was always confined to the Er-doped germanosilicate ring, i.e. within 3 μm under the anode surface. Clearly, the presence of the Er-doped ring must be responsible for trapping the SON layer.

The reason for Er doping having this trapping effect was proposed to be that the immobile Er³⁺ ions take up almost all the non-bridging oxygen (NBO) defect sites and thus block the migration of Na⁺ and H⁺ ions. An Er³⁺ ion has high electric field strength and requires six NBOs in the first coordination shell to screen its electric charge. As Na⁺ and H⁺ ions are also located near the NBO and need such interstitial regions in the glass network for migration. Er-doping in the same glass means that most of the Er³⁺ ions are inevitably situated in the migrating path of Na⁺ and H⁺ ions.

It is thus possible to modify the behaviour of poled fibres by creating internal structure with regions of different glasses. This would permit the localisation of the nonlinear region and potentially its stabilisation.

3.3 Interfaces and defects

The broader impact of the stress and defects in these interface regions may also be important. The models for poling almost exclusively, and invalidly, assume that the medium is homogeneous.

Time evolution for durations substantially in excess of 60 mins, when the main SON layer had completely migrated from the anode to the cathode, showed (Fig. 13) sections of the core-cladding interface almost parallel to the poling direction had become SH active. This phenomenon is a direct result of thermal poling, as no SH signals from the core-cladding interface of un-poled samples were observed.

Since the main SON has long passed by, it must be assumed that the injected H⁺ has also passed by, so presumably another mechanism is involved. Differences in thermal expansion coefficients between core and cladding glasses in the fibre-drawing process cause a strong stress gradient at the core-cladding interface, which could rupture Ge–Si or Si–Si wrong-bonds with ejection of an electron to form GeE’ or SiE’ centres, SiO³⁻, and subsequently drawing-induced defects (DID) through recapturing electrons at SiO³⁻ sites accompanied by a local structural relaxation. During thermal poling, excited by heating and driven by the poling electric field, the recaptured electrons on DID centres may escape and migrate along the poling direction using neighbouring SiO³⁻ sites as “stepping stones.” In this way, the separated electrons and SiO³⁻ sites can establish a space-charge field along the two interface sections that are nearly parallel to the poling field. This process does not depend on the migration of Na⁺ ions, so if this is
the correct explanation it suggests that a space-charge field could be established in purer glasses in which no mobile alkali ions are available. The magnitude of the SON at the core-cladding interface was measured to be \( \sim 0.05 \) pm/V, which is substantially smaller than that normally induced.

The above work prompted the investigation of glasses with essentially no mobile ions. A twin hole fibre was fabricated where the cladding glass between the two holes was “pure” silica synthesized by the MCVD process. Typical SH micrographs from a fibre sample poled for 15 min are shown in Fig. 14. As expected, considering that the silica being poled was very pure, no layer-shaped SON distribution was observed. Instead, very weak SON was formed directly on the inner surface of the anode hole due to the accumulation of surface charges as a result of thermal poling.

The interesting feature is that part of the core–cladding interface became SH active. The two SH-active interface sections are nearly parallel to the applied poling field, as shown in Fig. 14a. Careful examination of the polarization dependence of the SON at the two sections revealed, surprisingly, that the frozen-in space-charge field was mainly along the direction perpendicular to the poling direction. The effective nonlinear coefficient at the SH-active interface sections was measured to be around 0.05–0.1 pm/V. Further experimental analysis confirmed that the SH signals were found to be distributed in two parallel lines with a separation of 3.7 \( \mu \)m at the points with the highest SH intensity, a spacing very close to the core diameter in the direction perpendicular to the poling direction. The effective SON was measured to be 0.058 pm/V.

The location of the induced SON, and the absence of mobile alkali ions, again suggests electrons from defects at the core-cladding interface are involved. That the major component of the SON is perpendicular to the applied field direction is unexpected and there is currently no compelling explanation. It might be argued that, since the wrong-bonds rupture occurs along the core radial direction for stress release, the resultant space charge field would be predominantly formed along this radial direction, thus explaining the unexpected directionality of the dependence of the SH signal on the polarisation of the fundamental laser beam.

Clearly the presence of defects at the core cladding interface should not be ignored when considering poling of waveguides, as opposed to bulk glass. Different mechanisms may be involved, and in some circumstances may dominate.

4. Laser assisted poling

4.1 CO2 laser poling

In 2001, Blazkiewicz et al. used a CO2 laser as the heat source in thermal poling. It has several advantages including rapid and localized heating. The localisation permits periodic poling for QPM SHG devices. The rapid heating might permit poling the fibre during the draw process.

Silica absorbs CO2 laser radiation well; hence the heating of the fibre surface is rapid. A Bragg grating was used to determine the core temperature for various laser powers and dwell times. The 3 mm laser beam was scanned, orthogonal to the field direction, along a 7 cm length of twin hole fibre after the poling voltage had been applied. As shown in Fig. 15, initially the LEO coefficient was zero, jumping to \(-0.2\) pm/V when the poling voltage was applied. As the laser was scanned along the fibre, the measured total LEO increased steadily to \(-0.8\) pm/V, where it remained when scanning ceased. When the poling voltage was subsequently removed the LEO drops to \(-0.4\) pm/V.

The impact of scanning rate was assessed for a beam irradiance of 50(\pm 2) W/cm^2. The induced LEO increased with increasing dwell time (the time that the laser spot irradiates any point as it scans and hence inversely proportional to scanning speed) up to a certain point, after which it plateaued (Fig. 16). The minimum necessary dwell time was 0.55 s. This very fast poling is technologically important and scientifically interesting because it is several orders of magnitude faster than “standard” thermal poling using a heater. Since the CO2 laser radiation is simply a heat source, this is an anomaly that remains unexplained; perhaps the very much more rapid heating, or the directionality of the heating, are important.

4.2 UV poling

In 1994, Fujiwara et al. demonstrated significantly increased LEO using UV-laser poling. A typical twin-hole fibre was irradiated with 36 mJ/cm^2 pulses from a 193 nm excimer laser whilst applying \(-100\) V/\(\mu\)m. The evolution of induced \( V_{zL} \) with exposure (Fig. 17) shows a saturated TE value of 32 Vcm, which cor-
responds to an induced electro-optic coefficient of 6 pm/V. Note also that there is an approximate factor of three difference between the TE and TM responses. This is as expected from theory (for a bulk EO material), but almost never observed for thermally poled fibres. Measurements were also performed at 5 MHz (the limit of the experimental equipment available), producing near identical values of $V_\pi L$.

A significant advantage of the UV-poling processing technique is the ability to periodically pole the fibre to produce electrically tunable in-fibre Bragg gratings by introduction of a phase mask in the UV writing beam.\textsuperscript{56} The transmission spectra for a typical poled grating with varying applied (modulating, not poling) voltages is shown in Fig. 18. The reflectivity and reflection wavelength can be electrically tuned. Clearly, such an electrically tunable wavelength selective device would have many potential applications.

These very exciting initial results were dogged by poor long-term repeatability. Essentially identically made preforms would behave very differently. This difficulty has resulted in this aspect of poling being largely abandoned. The source of this variability has never been explicitly identified; however the next section throws some light on the probable cause.

5. Structural changes

The discussion of the mechanism of poling so far has been of charge migration establishing an internal space charge field. This is widely accepted as the explanation in the great majority of circumstances for the poling of silicate glasses. However, there is important evidence of other more fundamental mechanisms in certain circumstances.

5.1 Modification of $\chi^{(3)}$

Xu et al. measured the D.C. electrical field induced linear electro-optic coefficient versus D.C. voltage and found evidence of modification of the $\chi^{(3)}$ (Fig. 19).\textsuperscript{57} For an unpoled sample the response was that of the applied electric field acting on the $\chi^{(3)}$: a linear relationship. For the poled sample the line displaced largely as expected: the LEO axis intercept (0.1 pm/V) giving the induced LEO and the applied voltage axis intercept (3 kV) corresponding to the internal, frozen-in field strength. However, the slope changed by a factor of more than two. Apparently, and unexpectedly, the $\chi^{(3)}$ had increased as a result of thermal poling. Interestingly, when the fibre was depoled by heating without an electrical field, redistributing the migrated ions, the LEO and frozen-in field returned to zero but the $\chi^{(3)}$ largely remained at the increased value.

Subsequently, similar investigation of UV-poled twin-hole fibre gave similar results but with an apparent factor of three increase in the $\chi^{(3)}$ (Fig. 20). It was less surprising that UV irradiation causes such a change, since the much higher energy involved could permit more fundamental changes than ion redistribution.
5.2 Field assisted crystallisation

In 1999, Matsumoto et al. suggested the $\chi^{(3)}$ change in UV poling resulted from micro-crystallisation, and presented experimental evidence for it using sections of optical fibre preforms made of germanosilicate glass. $\chi^{(3)}$ was measured before treatment and after UV poling at several different poling field strengths. The UV poling caused an increase in the $\chi^{(3)}$, but only for poling fields over the threshold value of $5 \times 10^6$ V/m (Fig. 21). X-ray Diffraction (XRD) measurements on the samples (Fig. 22) showed negligible difference between unirradiated glass and glass UV irradiated without an applied poling field. However, for the UV-poled glass a substantial feature indicated that crystallisation had taken place and it was suggested that the crystalline form was cristobalite. Microscopy revealed micron-sized domains had been created. The feature also had a threshold at $5 \times 10^6$ V/m.

This crystallisation provides a probable mechanism for the $\chi^{(3)}$ change in UV poling. Again, the repeatability was problematic with nominally identical fabricated glass samples (from VAD preforms) giving variable results and this line of research has not been continued to any significant level. The repeatability issues, as well as the $\chi^{(3)}$ change and large $\chi^{(2)}$, may result from this mechanism; perhaps due to a high sensitivity of the crystallisation to trace impurities or stress variations due to slight differences in thermal history.

In 2001 Cabrillo et al. made an interesting observation of crystallisation in thermally poled silica. TEM images indicated the formation of $\alpha$-cristobalite. Such a substantial change in the structure of the glass might account for the observed $\chi^{(3)}$ change. However it was nonetheless surprising that such changes could occur as a result of simply heating to a relatively modest temperature, albeit in the presence of an intense field. In 2003, Garcia et al. observed a factor of 1.9 increase in $\chi^{(3)}$ in thermally poled channel waveguides and ascribed it to changes in the glass matrix. $\chi^{(3)}$ was independent of the poling voltage.

Between 2004 and 2006, An and Fleming investigated crystallisation in thermal poling. Surface-polished fused silica discs, 30 mm across and 1 mm thick, were thermally poled for 60 minutes at 3.5 kV in air between an 8 mm diameter copper anode and a grounded 280°C aluminum heater. The poled disc was then cut into two pieces, exposing the sample cross-section that was parallel to the poling field; which was then polished. One sample was characterised using SH microscopy, while the other was etched in 10% (in volume) HF for 50 sec for Field-Emission Scanning Electron Microscopy (FESEM) characterisation.

The SH signal (Fig. 23a) shows a bright narrow line, corresponding to a well-defined SON spatial distribution. Figure 23b shows this SH image overlaid on the regular transmitted light image. The SON layer and the interface between the poled silica and the supporting glass slide can be clearly identified. Micrographs from the FESEM (Fig. 24) show a layer of etched sites, which consists of many tiny circular voids under the anode edge (Fig. 24a). The presence of such features indicates that structural change occurred within the poled silica. As the poled sample is fused silica with only trace impurities, such as alkali metal ions, phase separation is ruled out. An enlarged view of these features (Fig. 24b) shows they are ~17 nm. Considering Cabrillo’s earlier results, it was suggested that these etched voids were evidence of crystallisation: the voids were left when the crystals were preferentially etched away by HF acid. If this interpretation is correct, thermal poling had induced a ~660 nm thick layer, 5.7 μm from the anode, of nanocrystals, with a maximum size of ~20 nm.

Such nanocrystals were not found in samples that were just heated, thus thermal poling played an important role in their formation. It has been demonstrated theoretically and experimentally that an electric field can increase the nucleation rate and crystal growth rate by decreasing the critical radius of the nucleus and the free energy change required to form a nucleus.

![Fig. 21. Change in $\chi^{(3)}$ with UV poling.](image1)

![Fig. 22. XRD measurement of germanosilica before and after UV irradiation and poling.](image2)
of critical size. Using the relevant parameters for the cristobalite crystalline phase, the critical nucleus radius and critical electric field at 300°C can be estimated to be 0.91 nm and 1.5 × 10^9 V/m. The internal electric field can be estimated from the model, discussed in Section 1.3. Using Eq. (3), χ(2) of 1.0 pm/V and the χ(3) of fused silica of 2.0 × 10^-22 m^2/V^2, the frozen-in electric field can be estimated to be ~1.6 × 10^9 V/m.

The critical electric field is in strong agreement with the estimated frozen-in field suggesting that the strong internal electric field during poling causes nucleation at the poling temperature and these nuclei continue to grow into 10–20 nm sized crystal particles in the subsequent thermal poling process.

Comparison of the location of the SON and the nanocrystal layers revealed that the nanocrystal layer was located between the SON layer and the anode edge. 1.8 μm closer to the anode surface than the SON layer. That the nanocrystals layer is behind the SON layer may indicate that only in this region is the field between the injected charges and the depletion region sufficiently strong; perhaps reaching a maximum here in a balance between growth of the number of injected charges and the spreading out of those charges.

A sample was investigated to determine if the nanocrystals were SH active. The presence of the SON layer on another poled sample was first checked with SH microscopy. After it was depoled at 300°C for 30 min no SH signal was detected, indicating that the crystals are β-cristobalite, which are not SH active.

Field assisted crystallisation was also observed by An and Fleming in pure silica regions of thermally poled optical fibres (Fig. 25). The layer in this case was about 120 nm wide. The voids, like those observed in fused bulk silica, were in the range of 10–15 nm and of similar shape.

These latter results are strongly suggestive, but indirect. However there is a body of experimental evidence from several research groups and a reasonable theoretical explanation that supports an additional poling mechanism of field assisted nanocrystallisation. This is potentially very important as it may permit more substantial modification of the glass structure and properties than is available simply by charge migration.

6. Technological development

The potential poled increase in the χ(3) has prompted its use in fibre devices such as Optical Parametric Amplifiers. This however requires long lengths of poled fibre. Direct insertion of electrode wires into the holes in the fibre is impractical for lengths greater than ~1 m. In 1989, Li and Payne made 0.5 m devices by drawing molten gallium into the holes. In 2002, Fokine et al. made 22 m lengths using a bismuth tin alloy. A different approach involved depositing silver inside the holes via a chemical reaction between two liquids. These techniques are limited to the distance the liquid can be drawn through the holes.

A combination of two strategies was adopted to achieve...
greater length.21) The first part was the co-drawing of a wire electrode into a single hole fibre on the draw tower. The second part was the development of a conductive coating that could be applied to the fibre during drawing.67)

For co-drawing electrodes a special preform was prepared (Fig. 26a), with just one hole and mounted on a draw tower with a free-running spool of 50 μm diameter tungsten wire (Fig. 26b). Rapid oxidation of the thin wire at the high temperatures used in fibre drawing was avoided using a feed-through system that permitted the preform hole and wire to be in an inert (argon) atmosphere. Rugged fibre was drawn in lengths up to 200 m, limited only by the available preform length. 0.9 m of this fibre was poled with an applied voltage of 3 kV at 200°C (limited by the conductive paint used to provide the external electrode), achieving an EO coefficient, $r$, of 0.0125 pm/V. This relatively modest value presumably resulted from both the sub-optimal temperature and the much lower field strength across the core due to the geometry. This approach was improved by developing a conductive coating using a thermally cured polyimide loaded with between 2% and 10% of graphite flakes with sizes largely in the 10 to 20 μm range. These coatings had resistivities in the 1 kΩ/cm to 10 kΩ/cm region and were stable up to ~600°C. The field strength was improved using a modified D-fibre design with a trench in the flat close to the core.

The resulting fibre was poled with standard conditions. It quickly saturated to a modest EO coefficient of 0.085 pm/V. A sample of the fibre had the internal electrode removed and subjected to the extensive handling that manual electrode insertion entails and the electrode was reinserted after five days. The poling behaviour of the fibre was then found to be similar to standard fibre. It was postulated that the modest LEO in pristine fibre with co-drawn electrodes was a consequence of not introducing important impurities, such as atmospheric moisture or other impurities (perhaps sodium) that may be introduced by from handling. A similar effect has been observed in bulk glass.68)

This work demonstrated a viable technology for making very long lengths of poling fibre. However further work is required to elucidate the difference between the “pristine” fibre and fibre that has been exposed to more handling.

7. Applications

Whilst the major application driver for poling has been telecommunications, the rather low LEO attainable has resulted in really only one significant telecoms device demonstration, the EU GLAMOROUS 2 × 2 poled all-fibre switch.69) This switch was characterised in systems environments with no error penalty introduced when operating at up to 40 Gb/s. Also, error-free transmission was also demonstrated at 10 Gb/s using the device.
as a protection switch in a 820-km installed fibre link.

Despite the potential for poled SHG devices using the induced SON, there has been little work in this area, perhaps because of the need for Quasi Phase Matching using periodic structures. Recently there have been some impressive results70) that demonstrated 45 nm tunability through compressing the fibre. Conversion efficiencies for non-tunable fibre systems are in the 5–10% range, with predictions of 50%.71) For many potential applications the currently achievable levels of $\chi^{(2)}$ are inadequate and cannot be compensated practically by making the devices longer. However one application for which this is not a significant concern is voltage sensing in the electrical power industry. A sensor needs to measure the voltage of an electricity transmission line by determining the line integral of the electric field between the ground and the high voltage conductor. This application implicitly involves large voltages and long lengths and hence, within reason, is unaffected by modest levels of $\chi^{(2)}$.

Michie et al have been developing such a system; recently publishing results that are very promising.72) The system (Fig. 27) uses a poled fibre with LEO of ~ 0.16 pm/V which is helically wound since the longitudinal EO component is zero. The orientation of the fibre is critical and is maintained by a special design with two flats. A low coherence interferometric sensing system measures the small difference in electro-optic response between the two polarisation modes of the poled fibre.73) Whilst for a bulk uniaxial crystal a difference of 3:1 would be expected, in almost all twin hole fibre the response is much smaller, typically 1.15:1.74) The source was ASE from an EDF. The poled fibre was coiled around a 95 mm diameter, 500 mm long, cylindrical former and placed inside a high voltage test enclosure (~22 kV RMS at 50 Hz). The response is shown in Fig. 28 for averages over ten cycles and four seconds. The linearity between 2.5 kV and 12 kV RMS, where breakdown occurred, is good, particularly for the 4 s averaged values. The performance approaches the needs of energy metering applications and demonstrates the feasibility of this voltage sensor.

8. Conclusion and future directions

The development of the understanding and technology of poling over the last twenty years has been significant. However there is still plenty yet to be explained regarding the mechanisms and true commercial application is yet to happen.

We have a very good understanding of many aspects of the mechanisms involved. Heat makes ions mobile; they then migrate under applied electric field and on removal of the heat freeze in to give a space-charge field. This breaks the centrosymmetry of the glass and causes useful second-order nonlinearity and linear electro-optic behaviour. There is reasonable understanding of the charges involved in this process and the influence
of the glass and dopants on their mobility. For the most common materials we have a good understanding of the conditions necessary to optimise the poling process. However this is not the whole story. Experimental evidence indicates there is still more to be learned before we approach a full understanding.

A ~1:1.15 ratio, rather than 1:3 ratio, between $d_1$ and $d_3$ is widely reported, but remains unexplained. If the reason lies with the waveguide structure it may be controllable, opening the way for devices with polarisation insensitivity (or improvements in polarimetric systems).

There is strong evidence that the interfaces hinder the progress of the mobile ions, perhaps due to stress or defects or both. Furthermore, there are some poling effects unique to fibre core-cladding interfaces, perhaps due to electron migration between defect sites.

Laser assisted poling presents some particularly interesting questions. Firstly the rates involved in CO$_2$ laser poling are orders of magnitude faster than regular thermal poling, which is surprising since the CO$_2$ laser surely only heats the fibre. Most tantalising is the UV poling which demonstrated record EO coefficients, although identification of conditions for ready repeatability have proven elusive. Field-assisted crystallisation may be involved. This effect has also been observed in certain circumstances with thermal poling.

Understanding these aspects of poling should create significant opportunities. Structured glasses with multiple internal interfaces between differing materials may allow us to localise and stabilise the nonlinearity. Control of the field assisted crystallisation may permit us to engineer new materials with many of the desirable properties of glasses but with useful levels of nonlinear nanocrystals in waveguide cores.

There are significant potential applications for poled fibre technology. Even at the current level of development some applications appear commercially realistic. Further research has potential for commercially viable low cost modulators and tunable gratings for telecommunications, for new sensor systems and for practical new laser sources at wavelengths otherwise not readily available.

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References
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