Dynamics of the second order nonlinearity in thermally-poled silica-glass

D. Faccio, V. Pruneri
Corning-OTI R&D, Viale Sera 222, 20126 Milano, Italy

P.G. Kazansky
Optoelectronics Research Centre, Southampton University, Southampton, SO17 1BJ, UK

Abstract: We study the temporal evolution of the second-order nonlinearity in thermally poled silica-glass. Our results differ significantly from those reported so far for the ionic charge evolution and show strong dependencies on sample thickness.

© 2001 Optical Society of America
OCIS codes: (060.4370) Nonlinear optics, fibers; (060.2280) Fiber design and fabrication

Ever since its first demonstration, thermal poling as a means of inducing a second-order nonlinearity (SON) in glass has attracted much interest due to its potential applications in various optical devices. It is a well established fact that in glass the mechanism at the basis of SON formation is ionic migration and subsequent creation of a frozen-in internal electric field. However, theoretical modeling of field-assisted ion migration is rather complex and has been limited to one [1] or two species [2] whereas experimental evaluation of positive-ion movement [3] may not be sufficient to determine the exact internal electric-field profile. Here we investigate the temporal evolution of the nonlinear coefficient ($d_{33}$) and of the nonlinear thickness ($L$) in thermally poled silica using the noncollinear Makers fringes technique (NCMFT) which allows high resolution [4]. Samples of different thickness ($S$) were thermally poled for various poling times. The silica-glass samples were Herafil 1 grade (from Heraeus) with $S = 1, 0.5$ and 0.1 mm. Thermal poling was performed at $270^\circ C$ in air by applying a constant voltage ($V$) of 4 kV, using Al-evaporated electrodes, for seven different times ($t$): 2, 5, 10, 20, 30, 45 and 90 minutes. The samples were subsequently cooled to room temperature with the voltage still applied. Cooling from $270^\circ C$ to $300^\circ C$ (when poling effects become negligible) takes $\sim 40$ seconds.

The nonlinear depth was obtained using the NCMFT which allows non-destructive measurements of thicknesses as small as 2 $\mu$m with sub-micron resolution [4]. Two identical input fundamental beams are focused onto the sample with a relative 90$^\circ$ external angle. The power of the generated noncollinear second harmonic (SH) beam is measured as a function of the sample inclination angle and $L$ is estimated by fitting the spacing and position of the observed peaks with the function given in [4]. The measurements were carried out using a Q-switched and mode-locked Nd:YAG laser as fundamental source. A half-wave plate controls the polarization of the fundamental pulses before they are split by a 50% beam-splitter and focused onto the sample. The SH signal was measured with a photo-multiplier tube after eliminating the fundamental beam using broadband and interferometric filters. Figure 1(a) shows an example of the SH power as a function of inclination angle for a sample with $S = 0.5$ mm and poled for 10 minutes, along with the best fit obtained assuming a truncated-gaussian nonlinear profile $\propto (1-s/L)^2/L^2$ where $s(z)=1$ if $0 < z < L$ and is otherwise null and in this particular case $L = 3.4$ $\mu$m, as shown in the inset of the figure. The sharp decrease in the profile may be due to the presence of a thin charge layer. Once $L$ is known the nonlinear coefficient is found by normalising the collinear SH with respect to that from a reference sample (quartz) and assuming that the tensorial components of the nonlinearity $d_{33}$ and $d_{31}$ are related to each other by $d_{33} = 3d_{31}$. All measurements were made one hour after poling and then repeated a week later without observing any significant variation in the measured $L$ or $d$ values. Figure 1(b) shows the observed evolution of the nonlinear coefficient $d_{33}$. A fast initial increase is followed by a significant decrease to a final value which is roughly 50% smaller than the peak-$d_{33}$. Furthermore, the poling times for which the peak-$d_{33}$ values are observed decrease with decreasing $S$.

The main mechanism for the nonlinearity formation is thought to be electric-field induced ion migration - after cooling the sample and removing the electrodes an electric field ($E$) remains frozen in the sample that couples with the third-order nonlinearity to give an effective SON,

$$d_{33} = \frac{3}{2} \chi^{(3)} E$$  \hspace{1cm} (1)
where $\chi^{(3)}$ is the glass third-order nonlinear susceptibility and $E$ is the frozen-in electric field. The full equations which describe this process, considering both drift and diffusion, can be rather complicated and have been solved under simplified conditions. Von-Hippel [1] considered only one ion species drifting which, in our case, would be sodium ($Na^+$), the main charge carrier in silica-glass with mobility $\mu_{Na}$. As the thermally mobilised ions drift towards the cathode, two distinct regions form in the glass: a depleted region with negative space-charge followed by an un-depleted, neutral region. The depletion region forms under the anode with a monotonically increasing depth, until the equilibrium value $L_{eq} = \sqrt{2eV/\rho}$ is reached (where $\varepsilon$ is the glass dielectric constant and $\rho$ the depleted charge density). The internal voltage drop also increases with $t$ and the overall effect is an increase in the frozen-in electric field, i.e. in $d_{33}$, and the maximum value is reached at equilibrium. Therefore a one-charge carrier model cannot account for our experimental results which show a fast growth to a maximum followed by a slower decrease to smaller values.

The next most mobile charge carrier in silica glass is $H^+$ with a mobility ($\mu_H$) which has been found to be in the range $10^{-4}$ to $10^{-3} \mu_{Na}$. If press-contact or non-blocking evaporated electrodes are used, then hydrogen continuously diffuses under the influence of the externally applied electric field from the external atmosphere into the glass. Due to the fact that $\mu_H \ll \mu_{Na}$ three regions will form: straight under the anode a region with $Na^+$ substituted by $H^+$ - the charge in this region will depend on the amount of in-diffused $H^+$. This is followed by a negatively charged depletion layer and finally by the un-depleted neutral region. It is worth noting at this point that this model is still an approximation of the true situation. Indeed, the $Na^+$-depleted region is very different from the un-treated glass: the most mobile charge carriers have been removed and an electric field close to dielectric breakdown value is applied. Under these conditions a non-ohmic electronic current is to be expected. However, in its simplicity, the as-described two-charge carrier model provides a valuable insight to thermal poling.

The equations describing the process have been solved by Alley et al. [2] - the electric field inside the sample initially rises but is then followed, for longer poling times, by a decrease to smaller values. The nonlinear coefficient, proportional to the electric field, will follow the same evolution. It is worth noting that the above model describes thermal poling in air: poling in vacuum or with blocking electrodes shows a different behaviour [2, 5]. As we were able to ascertain using a similar model, the poling times for which the maximum $d_{33}$ values are obtained depend on many parameters, such as ion concentrations and mobilities which vary from glass to glass. Most importantly, there is a strong dependence on $S$ due to the higher electric-field values inside the thinner samples thus explaining the results in figure 1(b). Figure 1(b) also shows that there seems to be a minimum poling time below which no SH is observed (also observed in [2]). This minimum poling time is smaller than 40 seconds (necessary to apply the voltage and cool the sample) for $S = 0.1$ mm but increases to 5 minutes for $S = 0.5$ mm and to 10 minutes for $S = 1$ mm. Furthermore, poling at a higher temperature (e.g. $280^\circ$C) resulted in a shift of these threshold times to smaller values (2 minutes for $S = 0.5$ mm and 5 minutes for $S = 1$ mm). These results may be explained by assuming that the time required for a charge distribution to form, such that SH generation can occur, depends on both temperature and sample thickness (maybe due to a reduced mixed-ion mobility near the cathode [2]). By raising the temperature (i.e. ionic mobility) or decreasing the sample thickness (i.e. increasing the applied electric field) the necessary
charge distributions are achieved for smaller poling times.

Figure 2(a) shows the evolution of $L$ for the same samples of fig.1(b). The well-known continuous increase in $L$ is observed (see e.g. ref.[5]). The lines show the best fits for functions of the form

$$L(t) = L(0) + \alpha(1 - e^{-\beta t})$$

(2)

where $L(0) + \alpha = L(\infty)$ is the saturation value and $\beta$ is the growth rate. The observed evolution of $L$ differs (in particular for $S=0.1$ mm) from the measured positive ion-charge front evolution ($\propto \ln(t)$) [2] implying that the actual value of the nonlinear thickness may not correspond to that expected from these measurements. It is well known that a depletion region a few microns thick forms in the first seconds of poling [3] but we may infer from our measurements that another mechanism (maybe electronic migration) is necessary in order to also observe SHG and to explain the differences between positive-charge-distribution and SH measurements. Figure 2(a) also shows a marked dependence on sample thickness which may be qualitatively assigned to the different electric fields inside the samples.

Figure 2(b) shows the product $d_{33}L$ against poling time. The growth rates vary according to the sample thickness but the saturation value is roughly the same ($\approx 2.4\cdot10^{-18}$ m$^2$/V) for all $S$. This value may be used to estimate the $\chi^{(3)}$ using eq (1) and assuming that all the applied 4 kV voltage drops across the depletion region and remains constant. In this case we find $\chi^{(3)} = 4\cdot10^{-22}$ m$^2$/V$^2$, in good agreement with values estimated by other means [6].

References