Effect of Minority Species on Thermal Poling of Fused Silica Glasses

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High second-order nonlinearity (SON) in poled silica glasses [1] is of great interest for the development of linear electro-optic modulators and frequency converters monolithically integrated into optical fibres or planar glass waveguides. However, its origin [1, 2] is not fully understood. The extrinsic effects of poling time and voltage on second-harmonic (SH) generation in thermally-poled silica glass have been studied [1, 3]. In particular the quadratic dependence of the maximum SH signal on the applied voltage indicated linear dependence of the SON on internal electric field [3]. There are several studies on intrinsic effects associated with defects [1, 4] and minority species such as OH [1, 5] and Na [1, 6] in thermal poling of silica glasses. In this work we carried out a systematic analysis of oxygen related defects and impurities (OH and Na) in commercial fused silica glasses (without relying on their catalogue data) and discuss their effects on SON.

Table 1 shows the sample characterizations and the results of SH signal measurements in commercial fused silica glasses. We used three types of fused silica glasses, as in previous work [1, 4, 6]: electrically-fused quartz glass (type I), quartz glass fused in a H_2-O_2 flame (type II) and silica glass synthesized from $SiCl_4$ in a H_2-O_2 flame (type III). Two types of oxygen defects: oxygen deficient centre (ODC, ≡Si···Si≡) for type I and III silica and silicon lone-pair centre (SLPC, =Si:) for type II silica can be identified from the absorption bands near 5 eV [7]. The latter defect in Herasil 1 samples could be annealed out at 1000°C, which agrees with previous work [7]. The concentrations of OH were determined from the intensity of an infrared absorption peak at 3600 cm^{-1} using a molar extinction coefficient 86 $L \cdot mol^{-1} \cdot cm^{-1}$ for OH [8]. The concentrations of Na were analysed by the inductively coupled plasma (ICP)-mass method.

SH signal measurements were performed in bulk samples (15 x 15 x 3 mm) poled in air by applying 4 kV at 280°C for 60 min [3]. Q-switched and mode-locked Nd: YAG laser pulsed radiation at 1064 nm with an average power of 850 mW was used as the pump source. Laser radiation was passing through the samples at a Brewster angle of 60°. SH signals were detected by a Si detector and the value of SH signal in poled Herasil 1 samples was ~ 4.5 nW and the minimum detectable value of SH signals was about 0.1 nW. Our results in type I and type II silica glasses agree with previous results [1, 4-6]. However, no SH signal was observed in type III synthesized silica, contrary to previous studies [1, 6],where type III showed ~ 10 % of SH signal with respect to type I and II. Myers et al. [1] suggested that there is no obvious correlation between SON and Na or OH concentrations. Nasu et al. [5] concluded that the SH intensity is linearly dependent on OH concentration in all of the following three types of silica glasses: fused quartz, synthesized silica and sol-gel derived silica. Our results show that the SH signals are

independent of OH concentration and are observed only in fused quartz glasses (Infrasil 1 and Herasil 1) containing Na impurities in relatively-high concentrations, ≥ 0.4 ppm, according to the ICP-mass analysis.

Henry [4] showed that by using EPR analysis the SH signal in type I silica glass was independent of the relative concentration of Ge impurity E' defects sites, but that in type II silica glass was linearly dependent on this concentration. From our results in as-received (with the absorption band) and annealed (without the absorption band) Herasil 1 samples, one can infer that SLPC is not directly related to the SON in type II silica glasses.

Table 1 Impurity characterizations and SH signals in commercial fused silica glasses.

Type	Commercial Name	Defect	OH (ppm) catalogue	OH (ppm) analysis	Na (ppm) catalogue	Na (ppm) analysis	SH signals (a. u.)
I	Infrasil 1*	ODC	< 8	5	1	0.52	1.5
	IR**	None	8	<1	4	0.06	Not observed
II	Herasil 1*						
	As-received	SLPC	130~200	117	1	0.39	1
	Annealed	None		102			0.8
III	Suprasil 1*	ODC	1200	511	0.04	0.04	Not observed

* Heraseus, **Nippon Silica glass.

The effect of Na impurities on DC current measured during thermal poling processes was also studied. For this purpose circular electrodes of Au paste were formed and fired on both sides of the glass samples (10 x 10 x 3 mm). An Au grounded ring electrode was also formed on the cathodic surface to prevent effects associated with surface current.

Fig. 1 shows the DC current variation as a function of poling time at 280°C and 4 kV in type II silica, as-received Herasil 1, and in type III silica, Suprasil 1. The current in the former glass, which shows SON, decreases continuously and after ~30 min becomes approximately constant (Type I is similar to type II). This behaviour is similar to the electrical conduction attributed to trap filling processes in poling of nonlinear optical side chain polymers [8]. The type III silica glass, without detectable SON, has a similar behaviour; however, the magnitude of the DC current is about ten times smaller than that in type II silica glass. The difference between these two types of silica can be explained through the different concentration of Na impurities.

SH signals were observed in type I and II silica glasses poled above 200°C, with a maximum signal at ~ 280°C, in good agreement with previous results [1]. Fig. 2 shows the current variation during poling at two different temperatures (200 and 280°C) and 4 kV applied voltage for type II silica glass, as-received Herasil 1. The current at 200°C is small and constant in time. Therefore, the initial current decrease at 280°C is probably related to migration of mobile Na ions and formation of Na depletion region (poled layer). The relaxation time of current in Herasil

1 is consistent with the fact that the SH signal in this glass saturates after 45 min up to 180 min from the beginning of the poling process [3]. Our studies indicate that Na impurities play a key role in thermal poling of bulk fused silica.

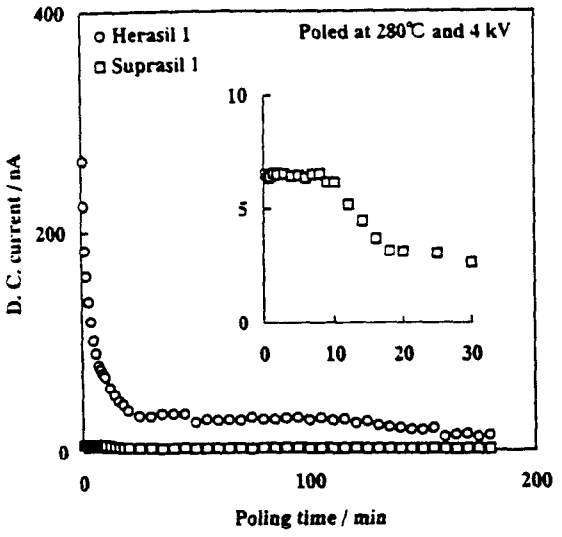

Fig. 1 DC current versus poling time in type II fused quartz and type III synthesized silica glasses at 280°C and 4 kV.

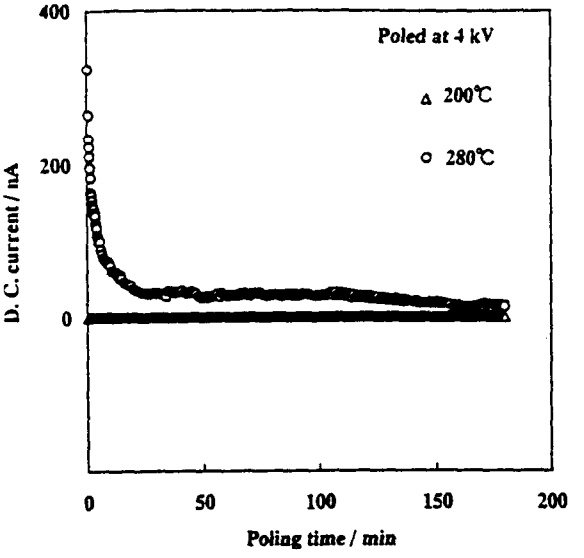

Fig. 2 DC current versus poling time in type II fused quartz glass, Herasil 1 at 200 or 280°C and 4 kV.

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