

# Humidity effect on the decay of second-order nonlinearity in thermally poled fused silica

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**Abstract:** Type I (GE124) and Type II (KV) fused silica were thermally poled in a vacuum and in air under identical poling conditions. Second-order nonlinear (SON) strength and nonlinear depth were found all to be the same. Samples were then stored in high and low humidity to study their SON stability. The SON of poled GE124 was stable over time despite different poling atmospheres and humidity in storage. The SON of both the air-poled and vacuum-poled KV samples decayed over time in both low and high humidity, with the exception that the air-poled KV sample stored in low humidity remained stable. High humidity accelerated the decay process of the KV samples. A porous surface model was used to interpret the decay mechanism. The decay curves implied multiple carriers or a multiple-porosity model for the decay mechanism.

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## 1. Introduction

Glasses belong to centro-symmetric structures. They inherently have no even-order optical nonlinearity. However, Myers *et al.* [1] discovered that thermal poling induced second-order nonlinearity (SON) in fused silica glass. They used Infrasil (Type I), Homosil, Optosil (Type II), and Suprasil (Type III) fused silica in their experiment and observed no decay of SON over several months. Later, Pruneri [2] thermally poled Herasil (Type II) fused silica glass in air and in a vacuum and got stable SON, they found that SON is stronger for air-poled samples, but the nonlinear profile is shallower. Many scholars have studied thermally poled glasses other than fused silica [3-8]. Although SON could be produced in these glasses, it decayed over time. For poled soda-lime silicate glass, decay of SON was observed in both water-saturated and dry conditions [3]. Decreasing alkaline ion mobility in the glass could enhance the stability of SON [9]. In this work we report the humidity effect on the relaxation of SON for Type I and Type II vacuum-poled and air-poled fused silica.

## 2. Experimental

We used two kinds of fused silica in our study. The first kind was Type I fused silica glass (GE124) supplied by General Electric, which is manufactured by electrically fusing natural quartz crystal. This type of fused silica has less than 50 ppm metallic impurities and less than 5 ppm hydroxyl (OH) content. The other kind was Type II fused silica glass (KV) supplied by Almaz Optics, which is manufactured by the flame fusion of natural quartz crystal. It contains metallic impurities of ~25–30 ppm and an OH component of ~400–500 ppm. Table I shows the impurity content of these two kinds of fused silica glasses from our own measurement. Trace element compositions were analyzed via inductively coupled plasma source mass spectrometry (ICP-MS) whereas the OH quantity was determined by infrared (IR) absorption spectrum.

We thermally poled samples in air and in a vacuum under the exact same conditions: heating in an evacuated chamber with the pressure below  $2.5 \times 10^{-5}$  mbar, or in air with the same heating rate to a stable temperature of 275°C. Then 5kV voltage was applied for 60 min., and then the samples were cooled to room temperature for ~6.5 h with the voltage still applied. The cooling proceeded through thermal conduction and radiation within the environment, and no water cooling was used. The cooling in the vacuum was very slow in our study, and we controlled the cooling rate in air to be the same as that in the vacuum with a programmable temperature controller. The samples were 14 mm<sup>2</sup> in size with a thickness of 1 mm.

We used the Maker fringe technique [10] to measure the nonlinear coefficient of the poled sample. During the measuring, the poled sample was rotated from  $-70^\circ$  to  $+70^\circ$  with its rotation axis parallel to the sample surface. Figure 1 displays Maker fringe patterns of both samples measured immediately after they were poled in the vacuum and in air.

To study the effect of humidity on poled samples, we stored the poled samples in wet (humidity  $> 90\%$ ) and dry (humidity  $< 10\%$ ) conditions, respectively. Only when the Maker fringe measurement was taken to monitor the variation of the second-harmonic (SH) signal of the poled samples did we expose the samples in room environmental humidity for  $\sim 40$  min. The angle of incidence of the Maker fringe measurement was fixed at  $\sim \pm 60^\circ$ , which corresponded to maximum SH signals.

Table I. Trace element composition of GE124 and KV glasses measured by ICP-MS. Structural OH impurities were measured by IR absorption spectroscopy.

Glass	Impurity content (ppm)											
	Al	Ca	Cr	Cu	Fe	K	Li	Mg	Na	Ni	Ti	OH
GE124	14	0.4	$< 0.05$	$< 0.05$	0.2	0.6	0.6	0.1	0.7	$< 0.1$	1.1	$< 5$
KV	1.3	10.3	0.1	0.2	$< 0.5$	6.2	0.6	0.8	19.2	0.2	$< 0.01$	400 ~ 500

### 3. Results and discussion

As shown in Fig. 1, the Maker fringe curves, obtained right after poling for the GE124 and KV samples, are nearly the same whether they were poled in vacuum or in air. Their second-order nonlinear susceptibilities  $\chi_{33}^{(2)}$  were found, with a simple step-like SON profile model, to be  $\sim 0.18$  pm/V and nonlinear depths  $L_n \sim 23$   $\mu\text{m}$ . It is obvious that directly after poling, vacuum and air-poled samples in our study show no difference in nonlinear strength and depth. These results seem to be inconsistent with Pruneri's claim [2] that the SH signals generated from samples poled in air are usually higher than those from samples poled in a vacuum and that the nonlinear depth in air is always shallower than in a vacuum for the same poling time. Pruneri *et al.* defined the poling time as the actual time at the poling temperature plus the cooling time to reach temperatures of  $\sim 220^\circ\text{C}$  [2], and they did not maintain identical cooling rates for both vacuum poling and air poling [11]. The poling time for vacuum and air poling in their experiment, strictly speaking, was not identical. But in our experiment, the cooling rates were maintained the same between vacuum and air poling, and owing to the slow cooling rate, the poling time was effectively longer.

Figure 2 shows the storage-time dependence of SH signals of poled GE124 samples stored in dry and in wet conditions, respectively. Error bars in Fig. 2 represent SH signal fluctuation in each measurement. There was  $\sim 20\%$  systematic error between measurements owing to the realignment of the sample when the sample was taken from storage and put on the Maker fringe setup. Figure 2 shows that the SH intensities were apparently stable over time, regardless of poling atmospheres and humidity conditions of storage.

Figure 3(a) shows the storage-time dependence of SH signals of KV samples poled in a vacuum (triangular mark) stored in dry conditions (open triangles) and in wet conditions (solid triangles). Figure 3(b) shows that of KV samples poled in air (square mark) and stored in dry conditions (open squares) and wet conditions (solid squares). For convenience of comparison, Figs. 3(c) and 3(d) are those curves of (a) and (b) but grouped by humidity. These figures show that the SH signal remained stable only in the case of air-poled KV

samples stored in dry conditions. For other cases, the SH signal decayed in storage regardless of the humidity.

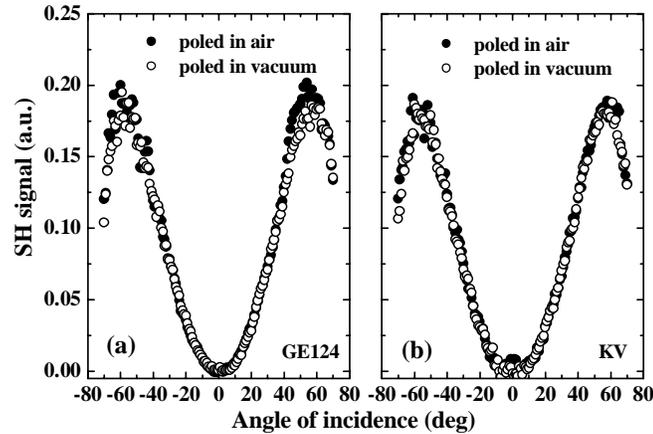


Fig. 1. Maker fringe curves of (a) GE124 and (b) KV glasses poled under vacuum (open circles) and in air (solid circles), respectively. The data were taken right after poling.

In order to analyze the decay characteristics, we applied the stretched-exponential function  $I(t)$ , sometimes known as the Kohlrausch-Williams-Watts (KWW) function [12,13], to fit the decay curves:

$$I(t) = I_o e^{-(t/\tau)^\beta}, \quad (1)$$

where  $I_o$  is the initial intensity,  $\tau$  is the relaxation time corresponding to the  $1/e$  intensity, and stretching index  $\beta$  stands for the deviation from simple exponential decay. In the case of  $0 < \beta \leq 1$ ,  $I(t)$  decreases monotonically, and in the case of  $\beta > 1$ ,  $I(t)$  remains one for a while and decreases from one to zero. In the case of  $0 < \beta \leq 1$ , Eq. (1) is the sum of several simple exponential-decay functions with various relaxation times [14]. In the case of  $\beta > 1$ , Eq. (1) is the sum of several step functions with a different width [14].  $\tau$  and  $\beta$  for each of the curves in Figs. 3(a) and 3(b) are shown in Table II.

It is obvious from Table II that high humidity accelerated the decay process with shorter relaxation time, whether the KV samples were poled in air or in a vacuum. While in low humidity storage, the air-poled KV sample was less susceptible to decay than the vacuum-poled KV sample.

The SON model first proposed by Stolen and Tom [15] is usually given to explain the SON induced in thermally poled fused silica (TPFS). The second-order nonlinear susceptibility  $\chi^{(2)}$  was correlated with third-order  $\chi^{(3)}$  by

$$\chi^{(2)} = 3\chi^{(3)}E_{dc}, \quad (2)$$

where the built-in electric field  $E_{dc}$  was believed [16] to be established in a positive/negative space charge on the anode side by a charge migration of anodic ions, e.g., mobile alkali ions ( $\text{Na}^+$ ,  $\text{Li}^+$ ,  $\text{K}^+$ ...) or  $\text{H}_3\text{O}^+$  ions, in the process of thermal poling. The nonlinear profile of TPFS could be determined by hydrofluoric (HF) acid etching [1,17], layer peeling method [18], and inverse Fourier transform technique [19]. The model proposed by Eq. (2) was supported experimentally. [20,21] Based on this model, we believe that the decaying of SON is caused

by the diminishing of the built-in field through migration and redistribution of the charged particles during storage.

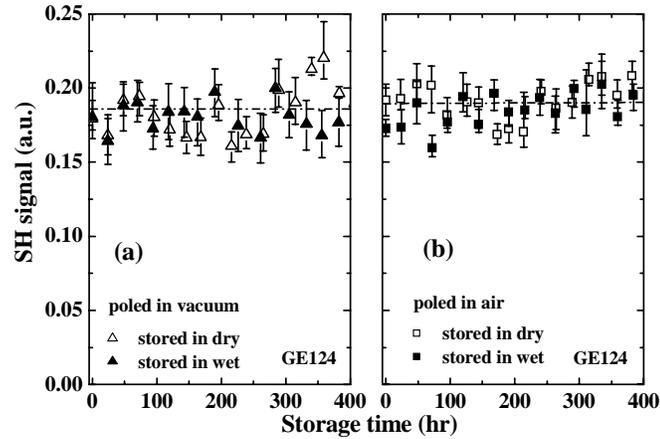


Fig. 2. SH signal as a function of storage time for (a) vacuum-poled and (b) air-poled GE124 glasses stored in dry and wet environments.

Garcia *et al.* [7] have postulated that the formation of a severe depletion region causes structural changes in glass with microfractures and densification, which make the glass surface porous. The porous surface of the glass facilitates channels for hydrogen/water to diffuse in the glass and diminishes the built-in field leading to the decay of the SH signal. Based on their postulates, we therefore believe that for the KV samples in our study, both air poling and vacuum poling create porosities in the surface, and the surface of vacuum-poled KV glass is more porous than that of air-poled glass. In high humidity storage, the more porous surface of the vacuum-poled sample will contribute to a diffusion of more hydrogen/water into the KV sample than into the air-poled sample. The diffused species of hydrogen/water are then ionized by the high  $E_{dc}$  near the anodic surface of the poled sample and recombine with a positive/negative space charge near the surface or within the bulk of poled glass. The strength of  $E_{dc}$  thus diminishes, and  $\chi^{(2)}$  decays at a higher rate. If the vacuum-poled KV glass is stored in dry conditions, the surrounding environment supplies less hydrogen/water; therefore, the SH signal of the sample stored in dry conditions decayed more slowly. On the other hand, the surface of the air-poled KV sample is less porous than that of the vacuum-poled one, so the amount of hydrogen/water diffused into the air-poled sample is small and the decay rate of the SH signal in air-poled KV glass is slower than that of the vacuum-poled glass. The SON of the air-poled KV sample is consequently stable when stored in dry conditions.

GE124 samples were stable with humidity as shown in Fig. 2. We may therefore assert, based on Garcia's postulates, that the surface of the poled GE124 samples were less porous than that of the KV samples. Since the major difference between GE124 and KV samples are their impurity contents and concentrations as shown in Table I, we therefore believe that the formation of a porous surface in the poling process is correlated with the impurity contents and impurity concentrations of the samples. Certain impurities and their concentrations seemed to favor the formation of a porous surface in the poling process. The major impurities that overwhelm in concentration for KV are Ca, K, Mg, Na, and OH. Also, we believe that the formation of a porous surface in which there are microfractures and density changes, as postulated by Garcia, is easier under lower atmospheric pressure.

As mentioned previously, if the parameter  $\beta$  is not equal to one, then depending on whether  $\beta$  is smaller than or greater than one, Eq. (1) represents a superposition of several

simple exponential or simple step functions with various time constants. As indicated in Table II, the parameter  $\beta$  is not equal to one for all cases. This fact implies that there is more than one kind of diffusing species, or more than one kind of micro porous network, associated with the decay mechanism of SON in poled KV glass. In the case of  $0 < \beta \leq 1$ , i.e., vacuum-poled KV glass stored in low humidity and air-poled KV glass stored in high humidity, the relaxation behavior of SON is the superposition of some simple exponential processes that are related to diverse ions with different mobility or to ions diffused through porous networks of different characteristics. For the case of  $\beta > 1$ , namely vacuum-poled KV glass stored in high humidity, step processes mathematically constitute decay actions of SON. The step process might correspond to a decay mechanism that is triggered by concentration of the species that accumulate to a threshold point. Although we are not able to identify the decay mechanism with a step process, nevertheless multiple carriers with different mobility or multiple porous networks with different characteristics are correlated with the decay of  $\chi^{(2)}$  in poled KV glasses as suggested by our data and analysis.

Table II. Relaxation time  $\tau$  and stretching parameter  $\beta$  obtained by fitting the stretched exponential function to the decay of SON in air-poled and vacuum-poled KV glasses at various humidity.

KV glass	Poled in vacuum		Poled in air	
	$\tau$ (hr)	$\beta$	$\tau$ (hr)	$\beta$
Stored dry	3282.9	0.3	$1.35 \times 10^{21}$	0.05
Stored wet	360.9	1.6	570	0.81

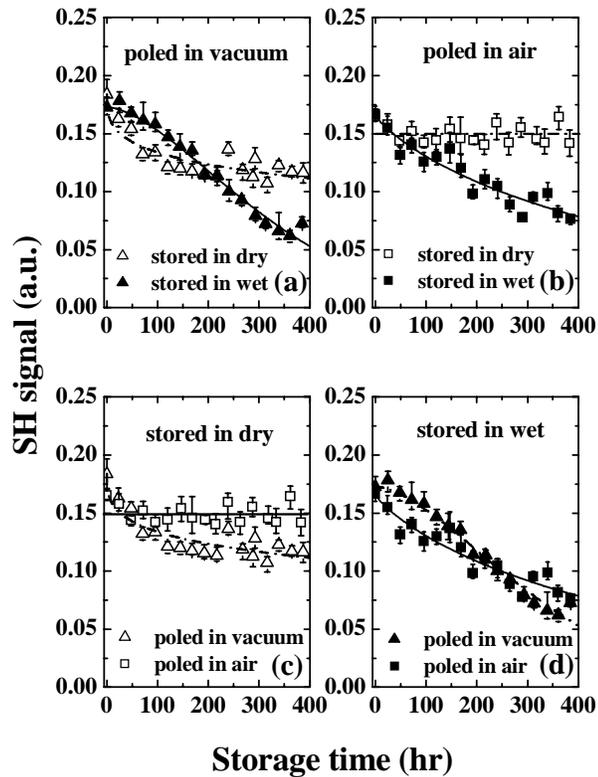


Fig. 3. SH signal versus storage time for (a) vacuum-poled and (b) air-poled KV glasses stored in dry and wet conditions. Dependence of SH signal on storage time for vacuum-poled and air-poled KV glasses stored in (c) dry and (d) wet conditions are also shown. Solid and dash-dot curves were fitted curves by a stretched exponential function.

#### 4. Conclusion

In conclusion, the induced SON of vacuum-poled and air-poled glasses make no difference in our poling condition of 5kV, 275°C, and 60 min. The SON of poled GE124 (Type I) glass is stable with time despite various poling atmospheres and humidity of the storing environments, while the SON of poled KV (Type II) glass decays with time except for air-poled KV glass stored in dry conditions. We believe these phenomena could be explained by the model of a porous surface that is created during thermal poling. Multiple species or multiple porous networks with different characteristics participate in the relaxation of SON. Low humidity suppresses the relaxation of SON in poled glass.

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