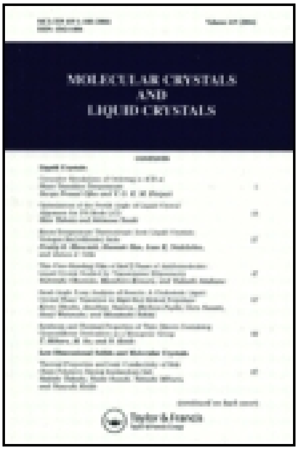

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Silica-Based Glasses as Photonic Materials –Second-Order Nonlinearity Induced by UV-Poling–

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After simultaneous applications of ultraviolet irradiation and a sufficiently high electric field, the so-called UV-poling, silica glass doped with germanium shows quite a large second-order optical nonlinearities in both bulk and film samples, and thus induced *d* coefficient is comparable to those of $LiNbO_3$ crystal. The induced effect decays after the UV-poling with exactly a single exponential function of time, suggesting a kind of ordered structure formed in the glass by the UV-poling. The decay rate strongly indicates Ge-E′ centers to be relevant agents to the nonlinearity. The decay or degradation can be made much slower with addition of impurities as electron scavengers. Mechanism to give the nonlinearity will be discussed, relating to generation of crystallites in the glass.

Keywords: silica glass; defects in glass; optical nonlinearity; SHG (Second Harmonic Generation); Ge-E′ center; crystallization in glass

INTRODUCTION

Development of active devices such as optical switches is essential for faster optical signal processings. Such devices inevitably require materials having the second-order optical nonlinearity, and they have so far been realized with various organic and inorganic crystals. However, crystal-based devices present some drawbacks such as appreciable production cost, non-negligible losses at interconnections with optical fibers due to differences of the thermal expansion, the refractive index etc., and cutting and polishing difficulties.

Glasses, especially silica and silica-based glasses, have in general advantages of wide transparent wavelength range, the capability to be shaped to any desired forms, durabilities against temperature variations and humidity, and others. And, glass-based devices have good connectivity to transmission network as the network is made of silica glass fibers. Glasses, however, possess the inversion symmetry which deprives them from the even-order optical nonlinearities, and therefore applications of glasses in photonics have been limited to passive functions.

In 1991, by applying a high electric field at elevated temperatures (the so-called thermal poling), Myers et al.[1] reported SHG (Second Harmonic Generation) of silica glasses with the *d* coefficient as large as 1pm/V.

Fujiwara et al.[2] then reported their pioneer work in 1995 that poling of Ge-doped silica glass together with UV-irradiation induces an electro-optic effect, much larger than any other techniques. The present authors and their coworkers followed this work, and by a number of studies,[3-5] they recognized the corresponding SHG in essentially the same kind of glasses.

Then, the research group has focused on elucidating the mechanism. And, on the way the group found a way to enlarge the magnitude of *d* coefficient. 5.1 pm/V is the largest magnitude so far achieved with a bulk 15.7mole%GeO_2-SiO_2 glass samples, and 12.5 pm/V with a film doped with 50 mole%GeO_2.

In this paper we will report on

(1) Magnitude
(2) Decay
(3) Enhancement
(4) Prolongation of decay or degradation
(5) Mechanism

of the induced nonlinearity in Ge-doped silica glasses.

EXPERIMENTAL PROCEDURE

Samples

Bulk samples were cut from preforms made by VAD method to 1x10x10 mm, and were polished to optical grade. All of the bulk samples used in this work were 15.7 mole%GeO_2-doped SiO_2.

Film samples of 1 micrometer thick were prepared by rf-sputtering on silica substrate at room temperature. Polycrystalline targets of $80SiO_2$-$20GeO_2$ and $50SiO_2$-$50GeO_2$ in mole% were used. Argon was used as the carrier gas and its flow rate was fixed at 3 cc/min. Flow rate of oxygen was varied in the range of 0 - 5 cc/min. Film thickness was measured by a surface profile-meter.

The films prepared in a mixed gas flow of Ar and O_2 were transparent and colorless, whereas those prepared in pure Ar were transparent but with a yellowish color which deepened as the thickness increased. Origin of this color has been attributed by Nishii et al.[6] to the formation of Ge^{2+} which has an intense absorption around 5 eV.

UV-Poling

With both bulk and film samples, UV-poling was carried out with an ArF excimer laser, which operated at 193 nm, has energy density of 100 mJ/cm^2 per pulse with pulse repetition of 10 pulses/s and pulse duration of 30 nsec. Total number of the shots for UV-poling was kept at 10^4 all the time during the work.

For poling the bulk samples, two electrodes were put into grooves made on two opposite sides of samples.[4] This construction was needed to avoid possible air breakdown at high electric fields. For poling the films, two Al electrodes were deposited on the same side, and then the electric field was applied in a vacuum, again to avoid air breakdown. The poling electric field strength was varied and *d* coefficient increased accordingly. See Fig.1.

Measurement of SHG and THG

Maker-fringe patterns were adapted to check any induced SHG, and THG (Third Harmonic Generation) if necessary. See Ref. [4], for example. The measurement was done at room temperature by using a Q-switched Nd:YAG laser, which operated with a fundamental wavelength of 1.06 μm. With both UV-poled bulk and film samples, the rotational axis for taking the Maker interference fringes was always chosen to be parallel to the direction of the poling electric field.

A Y-cut quartz with $d = 0.51$ pm/V was used as a reference to determine the absolute values of *d*.

Measurement of Optical Absorption

The measurement was carried out at room temperature by using a double-beam Shimazdu UV-2500 spectrometer. The wavelength ranged from 190 to 800 nm.

RESULTS

Magnitude of SHG

Magnitude of *d* coefficient depends on the poling electric field. In bulk samples it grows rapidly with increasing the poling field, and then saturates around 1.5 x 10^5 V/cm. Figure 1 shows the behavior, where d_{33} and d_{31} are the coefficients deduced from the Maker fringe patterns of s-s and p-s polarizations, respectively. Here, s-s and p-s mean relations of polarizations between fundamental-SHG lights. As expected, d_{33} is 3 times as large as d_{31} for all poling field strength, and the value exceeded d_{22} of $LiNbO_3$. Corresponding to the induced nonlinearity, the refractive index also shows the breaking of symmetry. Figure 2 is plots of n's of ordinary and extra-ordinary lights at fundamental frequency. Glass now shows the birefringence.

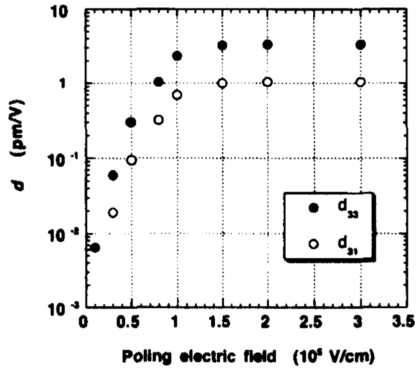

FIGURE 1 Poling field dependence of *d* coefficients in UV-poled glass.

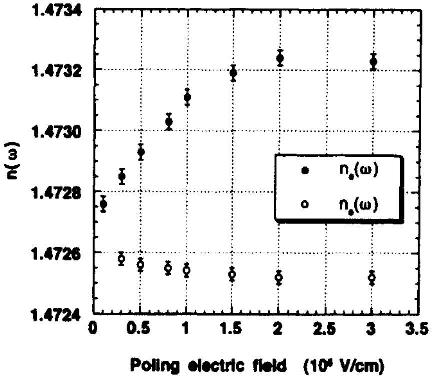

FIGURE 2 Poling field dependence of refractive indices for extra-ordinary (n_e) and ordinary (n_o) lights.

With film samples, two electrodes were put on the same side of films as was explained before, and direction of laser beam for the Maker fringe was always perpendicular to the poling field direction. The present authors measured d_{33} of the films using the fundamental light polarized parallel to the poling direction.

d coefficient of the films was found to depend on the gas flow content of O_2. Figure 3 shows its variation in samples of two different GeO_2 fractions as functions of O_2 flow rate. Definitely there seems to be an optimum content of O_2 around 1cc/min in both samples. At the optimum point, *d*'s are (3.3±0.2) and (8.7±0.4) pm/V, respectively, and the value seems to be proportional to GeO_2 content.

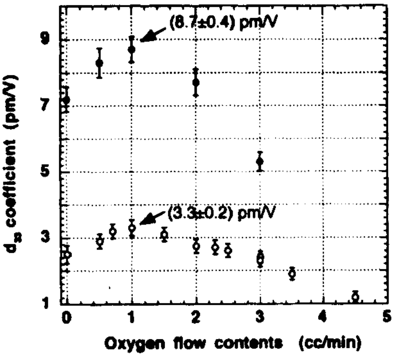

FIGURE 3
O_2 flow rate dependence of induced d_{33} in sputtered films.
GeO_2 in mole% : ○ (20)
● (50)

The appearances of SHG and birefringence are the direct indication of breaking of the inversion symmetry. This does mean that defect(s) formed by UV-poling should be very essential in the present matter.

Decay of the Induced Nonlinearity

The nonlinearity induced in the glass decays in general as a function of time after the poling. Figure 4 shows the decay of *d* coefficients at room temperature of various specimens, bulk and films. The decay time constant of the bulk sample at room temperature is approximately 280 days.

In all cases the decays are expressed exactly by single-exponential functions. This is very peculiar in glasses, and suggests existence of any "ordered" structure in UV-poled silica glasses.

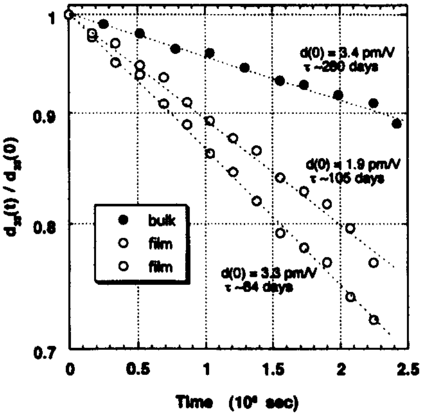

FIGURE 4 Decay behavior of d_{33} coefficients at room temperature of samples, bulk and films with different O_2 flow rate during sputtering.

The decay time constant of SHG in bulk sample, τ, obeys the Arrhenius equation,

$$\frac{1}{\tau} = \frac{1}{\tau_0}\exp\left(-E / kT\right) \qquad (1)$$

where E is the activation energy, T the temperature, and $1/\tau_0$ the pre-exponential factor. The value of E is (0.41±0.05) eV, as will be listed in Table I as "bulk (untreated)". See next section for "untreated" and "heat treated".

As was mentioned before, the nonlinearity is thought to be caused by defect(s) in the glass produced by UV-poling. Since these defects are color centers with their respective optical absorptions, one can correlate the behavior of nonlinearity to a particular defect or defects through the optical absorption. As a matter of fact, Fig.5 shows the Arrhenius plots of optical absorptions attributed to a number of defects in the glass, together with the variation of *d* coefficient. As is shown in this figure, the activation energy for the Ge-E' absorption, (0.40±0.10) eV, is in a marvelous agreement with the above-mentioned value. Therefore, we have succeeded to identify that the most relevant defect to SHG is Ge-E' center, which is a well-known defect in Ge-doped silica glass and consists of one Ge-atom associated with three O-atoms and one dangling bond.

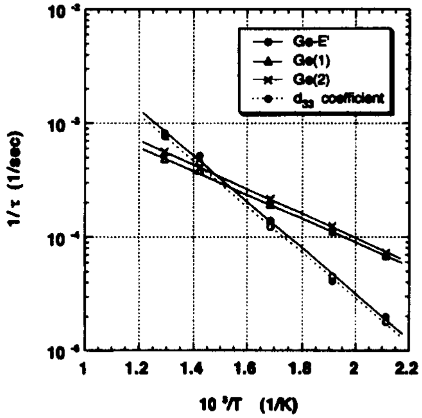

FIGURE 5 Arrhenius plots of induced defects and d_{33} coefficient. Ge(1) and Ge(2) denote electron trapped centers referred in [7].

Enhancement of the Nonlinearity

Ge-E' center is generated during UV-poling by the photo-chemical reaction,[7]

$$\equiv Ge-Ge\equiv \; + \; h\nu \longrightarrow Ge\text{-}E' + GeO_3^+ + e^- \qquad (2)$$

where the short bars on the right mean the bonds between Ge and O atoms. This equation means that the oxygen deficient defect on the left, the so-called neutral oxygen mono-vacancy (NOMV), does work as a precursor. Therefore, it is not a bad idea to increase number of the precursors to increase the nonlinearity. The present authors have tried the case, giving samples heat treatment at an elevated temperature in a suitable vacuum.[8]

Although conditions have not been optimized yet, we have achieved by this treatment to get a substantially larger *d* value than before. The largest value with bulk samples has been (5.1±0.2) pm/V, and that with sputtered films (12.5±0.6) pm/V.[9] The result is again an evidence that Ge-E' center is the key agent to bring the second-order nonlinearity. The activation energies of decay of *d* coefficient, optical absorption due to Ge-E' center and dark conductivity in samples with and without the heat treatment are listed in Table I.

TABLE I Activation energies of UV-poled glass

UV-Poled Glasses	Activation Energy (eV)
Decay of *d* Coefficient (SHG)	
bulk (untreated)	0.41±0.05
bulk (heat treated)	0.38±0.05
Defects	
Ge-E'	0.40±0.10
Dark Conductivity (see Fig.6)	
bulk (untreated)	0.44±0.05
bulk (heat treated)	0.37±0.05

Prolongation of Decay

The decay time constant with bulk samples at room temperature, 280 days, is of course too short for applications. The decay or the degradation should be in a sense much more important issue than the magnitude of *d* coefficient.

Look at the photo-chemical reaction, eq.(2), again. "Free" electrons are always produced during the reaction. The present authors have thought that the electrons are caught by some yet unknown traps for a while and then move back to their home sites, moving in the eq.(2) from its right to left sides.

This conjecture has been proved by dark conductivity measurement. The dark conductivity of UV-poled bulk samples were measured at various temperatures. Figure 6 then shows a summary of the result.[10] The activation energy to describe the Arrhenius behavior of the conductivity is again (0.44±0.05) eV for untreated sample, while the value is slightly smaller if the samples were heat-treated prior to UV-poling. Therefore, the decay or degradation of SHG is governed by the migration of free carrier, although we still do not know what the value, 0.4 eV, means.

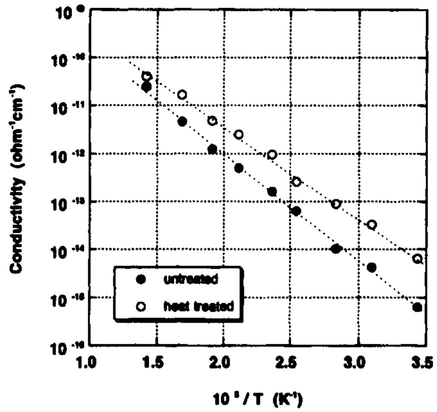

FIGURE 6 Temperature dependence of dark conductivity.

The present authors now propose that any dopant(s) which can scavenge the free carriers for a sufficiently long time should prolong the decay. As the first trial, they doped the glass with hydrogen, leaving samples in a pressurized hydrogen atmosphere for some days. The decay times with bulk and film samples loaded with hydrogen were both successfully made longer, as shown by the Arrhenius plots in Fig.7. The decay at room temperature is approximately 20 years with the bulk, and 7 years with the film. Conditions such as hydrogen content, loading condition and others have not been fully optimized yet, and we have various possibilities to improve things in the near future.

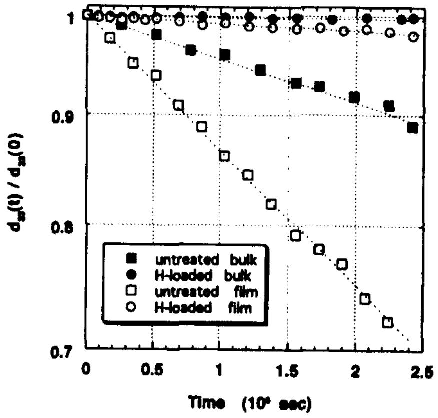

FIGURE 7 Arrhenius plots of normalized d_{33} coefficients in H-loaded glasses.

MECHANISM OF NONLINEARITY

The second-order optical nonlinearity induced in Ge-doped silica glass is quite relevant to the generation of Ge-E' centers, as the present authors have given various experimental evidences. Still we do not know how Ge-E' centers work to bring the effect or what the key role of Ge-E' centers in this matter is.

Two mechanisms have been thought.

One mechanism is that alignment of electric dipole moments of Ge-E' centers during UV-poling can give an anisotropy for the effect. This is possible but may not be large enough. The reasons are: (a) Increase of d as a function of the poling field, shown in Fig. 2, is obviously not expressed by the Langevin function. (b) As we know the number density of Ge-E' centers by ESR measurement, for example, we may estimate how large the dipole moment associated with one Ge-E' center should be. And, the magnitude seems to be too large.

The other one could be that an electric field is built up in the material during the poling, and the product of this space-charge field times the third-order nonlinear susceptibility of the system acts as an effective second-order nonlinear susceptibility. The third-order effect exists in any systems of even with the inversion symmetry.

Crystallization of Glass After UV-Poling

Surprisingly enough, crystallites have been found in UV-poled glass samples.[11] The crystallites appear if the poling field is beyond 0.5×10^5 V/cm. SHG also grows up at the same time beyond the same electric field strength. Figure 8 is the X-ray diffraction patterns of as-prepared, UV-irradiated, and UV-poled samples, where only the UV-poled sample shows the crystallization. The crystallites are more or less aligned probably to the direction of the poling field. The size seems to depend on the field strength.

Important point is that these crystallites did not seem to decrease or disappear even after SHG decayed out.

Crystal structure of the crystallites are being investigated.

Third-Order Nonlinearity

The present authors have measured the third-order nonlinear susceptibility in bulk samples of 15.7mole%GeO_2-SiO_2 glass, again by using the Maker fringe method. They have then found that $\chi^{(3)}$ increases by factor 15 if the samples are UV-poled. And moreover, the value do not decrease even if SHG decays at elevated temperatures. Therefore, such a large $\chi^{(3)}$ comes from the crystalline phase. The present authors claim that the decay of the induced nonlinearity is the decay of space-charge field.

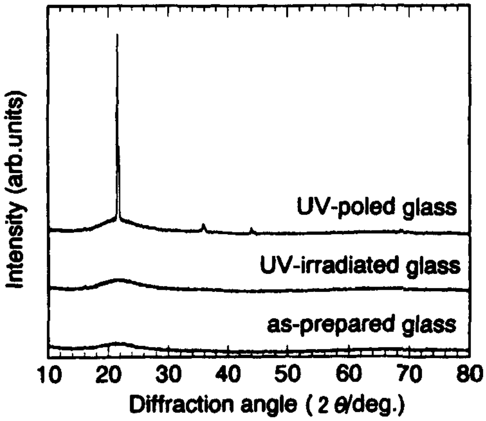

FIGURE 8 X-ray diffraction patterns.

CONCLUSION

A remarkably large second-order optical nonlinearity can be induced in Ge-doped silica glass, in its bulk and film samples. *d* coefficient to give SHG is already (5.1±0.2) pm/V in bulk 15.7 mole% GeO_2-SiO_2 samples, and (12.5±0.6) pm/V in film samples with 50mole% GeO_2.

The nonlinearity is quite relevant to the generation of Ge-E' centers during the UV-poling. Based upon the presently available knowledge, the present authors claim the following mechanism for the surprisingly large second-order nonlinearity in Ge-doped silica glass. The mechanism is that a space-charge field is built up in the glass by free carriers yielded during UV-poling, and at the same time crystallites having the third-order susceptibility of approximately 15 times larger than that of matrix glass are formed. Then, the space-charge field works as the second-order effect through this large third-order nonlinearity.

The decay or degradation of second-order nonlinearity is thought to be decay of the space-charge field, which is governed by the dark conduction of free carriers produced during UV-poling. The decay can therefore be very much reduced by adding any electron scavenger(s). Hydrogen seems to work nicely as one of such agents

Acknowledgments

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