Correlation of defect centers with second-harmonic generation in Ge-doped and Ge–P-doped silica-core single-mode fibers

T. E. Tsai

GEO Centers, Inc., Fort Washington, Maryland 20744

M. A. Saifi

Bell Communications Research, Red Bank, New Jersey 07701

E. J. Friebele and D. L. Griscom

Naval Research Laboratory, Washington, D.C. 20375

U. Österberg

University of Arizona, Tucson, Arizona 85721

Received March 13, 1989; accepted June 19, 1989

The origin of frequency doubling in Ge-doped silica-core single-mode glass fibers has been investigated with electron-spin-resonance spectrometry. Correlations have been observed between the conversion efficiency and the light-induced Ge E′ center concentration.

Österberg and Margulis[1] described a remarkable discovery that high-efficiency (>5%) second-harmonic generation (SHG) can be induced in Ge–P-doped silica-core single-mode fibers exposed for several hours to high-intensity (=40 kW peak power) pulses from a mode-locked Q-switched Nd:YAG laser operating at 1060 nm. For both scientific and technological reasons the observed phenomenon is of considerable interest. SHG generally requires a crystal structure that lacks a center of inversion. For efficient SHG, an additional criterion is phase matching between the fundamental and second harmonic to obtain long interaction lengths. This condition can be satisfied in birefringent crystals by proper polarization of the fundamental and the second harmonic.

Since amorphous materials do not possess long-range order, glass fibers would not be expected to exhibit second-order nonlinearity. Furthermore, dispersion between the fundamental and its second harmonic would seem to rule out satisfying the phase-matching conditions. Since the Österberg–Margulis report, many experiments have been carried out to understand the SHG phenomenon. Several models have been proposed to explain the second-order susceptibility in the glass fibers and how the phase-matching conditions are satisfied.

There is now fair agreement that the second-order nonlinearity is associated with some microscopic aspect of glass structure, such as defects[2,3] or alignment of some dipole-bearing molecules.[4,5] That phase matching is achieved through a self-written grating[2,4] is well established. However, the exact nature of the defects or the molecules responsible for the second-order nonlinearity have not been unequivocally identified. Two models[2,4] have been proposed to explain the origin of the self-induced grating. The first model[4] relies on nonlinear-optical interactions to generate high-energy photons and dc fields to align the defects. Stolen and Tom[4] found that with the presence of externally generated second-harmonic seeding light along with its fundamental, the preparation time for efficient SHG could be reduced from several hours to several minutes. In their model the 1064-nm pump light and the 532-nm harmonic light mix through the third-order optical susceptibility, $\chi^{(3)}$, generating a dc polarization field. This field is of the order of 1 V/cm and is of the right periodicity to create a phase-matching grating by aligning already-existing dipoles (defects) in the fiber. The remarkable reduction of preparation time has been a great success of this model. However, if such weak fields could align the dipoles, what keeps them aligned against normal room-temperature thermal agitation? Furthermore, permanent and much greater (though not phase-matched) enhancement in $\chi^{(2)}$ should be possible by applying a large external field.

Two experiments have been carried out to test the validity of the dc-field-induced permanent $\chi^{(2)}$. Mizrahi *et al.*[6] applied dc fields as high as 10 kV/cm to a slice of Ge–P-doped silica-core glass preform and monitored the SHG with a 1060-nm probe beam. On application of the dc field they observed weak SHG, which decayed to the zero level on removal of the field. They concluded from this that fields as high as several kilovolts per centimeter did not induce *permanent* $\chi^{(2)}$ in the glass. In another experiment, Bergot *et al.*[7] used single-mode fibers with built-in capillary electrodes to measure $\chi^{(2)}$ induced under a high externally applied dc electric field and 488-nm optical radiation. With dc fields as high as 200 kV/cm and a radiation

0146-9592/89/181023-03$2.00/0

density of 5 MW/cm^2, the measured induced $\chi^{(2)}$ was 7 $\times$ 10^{-4} m/V. This combined dc-field-induced and light-induced $\chi^{(2)}$ was permanent, except that it could be erased with intense blue light.[8] As they point out, this field-induced $\chi^{(2)}$ is nearly 100 times that achieved by the seeding process for SHG. These and other experiments have established that the $\chi^{(2)}$ associated with SHG is related to some defect structure in glass.

Lawandy[5] proposed that preexisting dipoles in the form of GeO molecules are oriented by the optical pumping field through a self-organization process to form second-order susceptibility gratings. This model predicts that a fiber with a higher concentration of GeO will have a higher SHG conversion efficiency. Yuen[9] has reported that the concentration of GeO is greater in Ge-doped silica than in Ge–P-doped silica prepared under the same processing conditions. However, in contrast to the predictions of the Lawandy model, the highest SHG efficiency (~13%) reported so far is in Ge-doped fibers with P as a codopant.[10]

Another model[2,3] postulated that the induced second-order susceptibility is associated with the dipoles of color centers created spatially periodic along the fiber by the high-power pumping light. Experiments consistent with this color-center model have been reported.[6,11,12]

To determine experimentally if SHG is accompanied by paramagnetic color-center formation, we have carried out electron-spin-resonance (ESR) studies on a number of single-mode fibers showing varying degrees of SHG conversion efficiency. Both Ge-doped and Ge–P-doped silica-core fibers were studied.

The samples were made of bundles of approximately 1-cm lengths cut from fibers with SHG treatment and from the corresponding unexposed reference fibers. ESR spectra were obtained on a Bruker ER 200D-SRC spectrometer operating at approximately 9.4 GHz and employing 50-kHz field modulation at relatively high modulation amplitude (0.63 mT) and microwave power (20 mW). For maximum single-sweep sensitivity, the lock-in amplifier was set to detect ESR responses at the second harmonic of the modulation frequency. However, absolute spin concentrations were determined by signal averaging in the normal first-derivative mode using 100-kHz field modulation and synchronous detection with the same modulation amplitude (0.63 mT) and lower microwave power (0.2 mW). The sample temperature was maintained at 110 K by means of a modified Bruker flow-through device.

In both Ge-doped and Ge–P-doped silica-core fibers, we observed Si E′, Ge E′, and H-associated centers. In the usual case, an E′ center consists of a hole trapped at an O vacancy in the glass network.[13,14] A Ge E′ center therefore is a positively charged point defect comprising an O vacancy at a Ge site. If we assume a net charge neutrality, for each E′ center there must exist a trapped electron somewhere in the material. Long-range electric fields associated with these defect centers may arise if the centroid of the trapped holes is different from the centroid of the trapped electrons. No P-associated centers[15] were

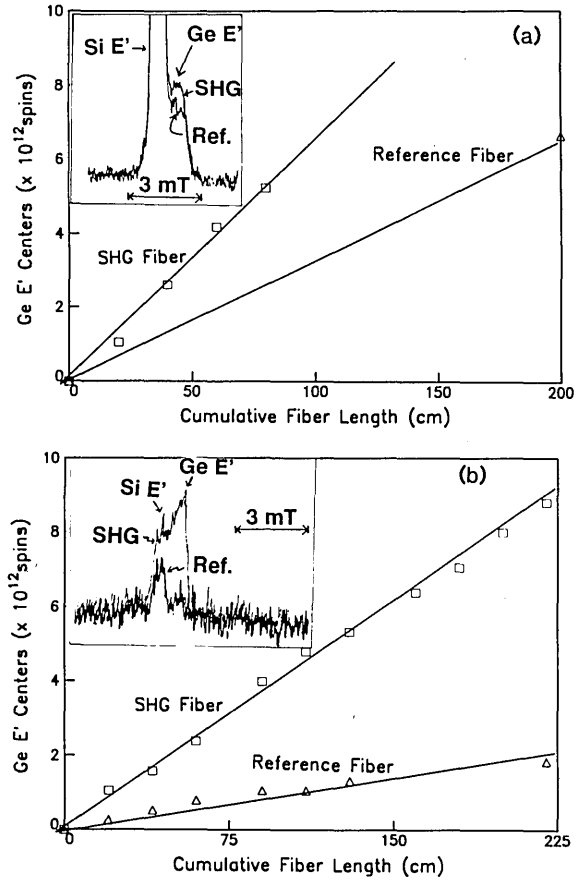

Fig. 1. Number of Ge E′ centers in (a) Ge-doped and (b) Ge–P-doped silica-core single-mode fibers as functions of the cumulative distance from the input end of a SHG fiber and an unexposed reference fiber. The insets show ESR spectra of Si E′ and Ge E′ centers taken in the second-derivative mode. The fiber in (b) is the original Stockholm fiber described in Ref. 1. Note that the ESR measurements reported here were carried out more than 3 years after the fiber generated second-harmonic light.

observed in the Ge–P-doped fiber either before or after SHG treatment. No differences in the concentrations of Si E′ or H-associated centers were observed between SHG fibers and the corresponding reference fibers of the same length, although the concentration of (preexisting) Ge E′ centers was much less in the Ge–P-doped fiber relative to the Ge-doped fiber [see the insets of Figs. 1(a) and 1(b)]. However, the concentration of Ge E′ centers was found to be consistently higher in the SHG fibers than in the reference fibers (Fig. 2). This difference increases with increasing length of fiber introduced into the microwave cavity of the spectrometer (Fig. 1). This result shows that our experimental signal-to-noise ratio is adequate to measure the induced Ge E′ centers in fiber lengths as short as 20 cm and that these centers are uniformly distributed along the fiber length. Table 1 shows that the fractional increase in Ge E′ concentration seems to correlate with SHG conversion efficiency.

This correlation suggests that the second-order susceptibility grating induced by the pump light is associated with paramagnetic Ge E′ centers. As reported by Österberg and Margulis,[16] the decrease in SHG conversion efficiency when SHG fibers are not used for a

few weeks is consistent with our results, since Ge E′ centers in irradiated Ge-doped silica are known to decrease owing to isothermal annealing.[13] The report of Saifi and Andrejco[3] that no SHG can be induced in Ge-free P-doped silica-core fibers is also consistent with our observation.

The initial concentration of Ge E′ centers in the Ge-doped reference fibers is found to be higher than that in the Ge–P-doped reference fibers (see Fig. 1), even though the Ge–P-doped fiber has a higher SHG conversion efficiency and higher fractional increase in Ge E′ centers after SHG treatment. These observations suggest that only those Ge E′ centers generated in the SHG treatment take part in the induced *permanent* second-order susceptibility. The preexisting Ge E′ centers do not contribute to the conversion efficiency of the SHG fibers (and may subtract from it) because they are not organized to have phase matching between the fundamental and second-harmonic light. This conclusion is consistent with the report in Ref. 10 that preannealing of Ge–P-doped silica-core fiber increases the SHG conversion efficiency 10 times, since the preexisting unorganized Ge E′ centers can be annealed out so that a higher fraction of the total Ge E′ centers can be induced and organized in the SHG treatment.

Figure 1 also shows that the induced Ge E′ centers are distributed throughout the whole length (~2 m in this case) of the SHG fibers, in contrast with reports that second-harmonic light is generated in the 10–40 cm of fiber nearest the injection end.[2,16] However, no contradiction is implied, since 10–40 cm is the coherence length due to the spectral bandwidth of the pump and input second-harmonic pulses.[17] Those Ge E′ centers induced beyond this region cannot organize themselves to phase match the fundamental and second-harmonic light.

In summary, we found that the SHG conversion efficiency in Ge-doped and Ge–P-doped fibers is correlated with the induced Ge E′ center concentration. The higher SHG conversion efficiency observed in Ge–P-doped fibers relative to Ge-doped fibers may be related to our observation that fewer Ge E′ centers are present in as-drawn Ge–P-doped fibers (see the insets of Figs. 1 and 2). Thus a higher fraction of the total Ge E′ centers can be induced in the SHG treatment of Ge–P-doped fibers. Preliminary studies exposing a Ge–P-doped silica preform to the third- and fourth-harmonic wavelengths of 1060-nm light (λ = 351 and 248 nm generated by an excimer laser) indicate that the fourth-harmonic light is probably responsible for the generation of Ge E′ centers. These and other aspects, such as the possible role of other Ge-associated defect centers [e.g., Ge(1) and Ge(2) centers[13]] in the SHG of Ge-doped and Ge–P-doped fibers are currently under investigation and will be reported in future publications.

We thank M. J. Andrejco for providing some of the fibers and preforms used in this study and C. C. Harrington for developing the software for ESR signal averaging.

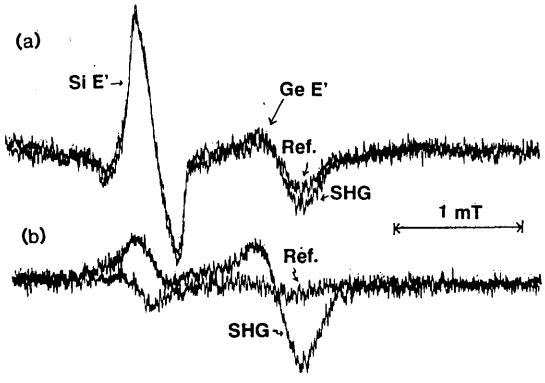

Fig. 2. Signal-averaged (10 sweeps) first-derivative ESR spectra of (a) Ge-doped and (b) Ge–P-doped silica-core single-mode SHG fibers and unexposed reference fibers recorded at 120 K with a modulation amplitude of 0.63 mT and a microwave power of 0.2 mW.

Table 1. Fractional Increase in Ge E′ Center Concentration and SHG Conversion Efficiency in SHG Ge-Doped and Ge–P-Doped Silica-Core Fibers

Group of Fibers	Fractional Increase (Ge E′)	Conversion Efficiency (%)
Ge–P doped	3.4	5
Ge doped no. 1	0.96	1.5
Ge doped no. 2	0.20	≈0.5

References

1. U. Österberg and W. Margulis, Opt. Lett. **11,** 516 (1986).
2. M. C. Farries, P. St. J. Russell, M. E. Fermann, and D. N. Payne, Electron. Lett. **23,** 322 (1987).
3. M. A. Saifi and M. J. Andrejco, Opt. Lett. **13,** 773 (1988).
4. R. H. Stolen and H. W. K. Tom, Opt. Lett. **12,** 585 (1987).
5. N. M. Lawandy, "Mechanism for efficient second-harmonic generation and the formation of Hill gratings in germanium-doped fibers" (submitted to J. Opt. Soc. Am. B).
6. V. Mizrahi, U. Österberg, J. E. Sipe, and G. I. Stegeman, Opt. Lett. **13,** 279 (1988).
7. M.-V. Bergot, M. C. Farries, M. E. Fermann, L. Li, J. Poyntz-Wright, P. St. J. Russell, and A. Smithson, Opt. Lett. **13,** 592 (1988).
8. M. C. Farries, Department of Electronics and Computer Science, University of Southampton, Southampton S09 5NH, UK (personal communication).
9. M. J. Yuen, Appl. Opt. **21,** 136 (1982).
10. M. C. Farries, in *Proceedings of Colloquium on Nonlinear Optical Waveguides* (Institution of Electronics Engineers, London, 1988).
11. M. C. Farries and M. E. Fermann, Electron. Lett. **24,** 294 (1988).
12. B. Valk, E. M. Kim, and M. M. Salour, Appl. Phys. Lett. **51,** 722 (1987).
13. E. J. Friebele and D. L. Griscom, in *Defects in Glasses* (Materials Research Society, Pittsburgh, Pa., 1986), p. 319.
14. D. L. Griscom, in *Defects in Glasses* (Materials Research Society, Pittsburgh, Pa., 1986), p. 213.
15. D. L. Griscom, E. J. Friebele, K. J. Long, and J. W. Fleming, J. Appl. Phys. **54,** 3743 (1983).
16. U. Österberg and W. Margulis, Opt. Lett. **12,** 57 (1987).
17. H. W. K. Tom, R. H. Stolen, G. D. Aumiller, and W. Pleibel, Opt. Lett. **13,** 512 (1988).