Effect of Ionizing Radiation on *In Situ* Raman Scattering and Photoluminescence of Silica Optical Fibers

T. G. Bilodeau, K. J. Ewing, G. M. Nau, and I. D. Aggarwal

Abstract—**Raman fiber optic chemical sensors provide remote *in situ* characterization capability. One application of Raman fiber optic chemical sensors is the characterization of the contents of nuclear waste tanks. In these tanks it is expected that approximately 20 meters of optical fiber will be exposed to radiation levels between 100 and 1000 rads/hour. In support of this work two silica optical fiber types (one a communications grade fiber and the other nominally radiation resistant) have been tested at the radiation levels expected in the tanks. Luminescence and Raman scattering measurements have been performed *in situ* with 488-nm excitation on two types of silica optical fiber exposed to a constant low to moderate dose rate of gamma radiation of 880 rads(Si)/hour from a ^{60}Co source for a total dose of greater than 45 krads. The nominally radiation-resistant fiber was also excited with 514.5-nm and near-infrared 830-nm laser radiation. The rate of the silica Raman signal fdecrease is more than three times greater for the visible excitation wavelengths than for the 830-nm excitation for the radiation resistant fiber. The behavior of the 650-nm photoluminescence line upon irradiation was different for the two fibers studied, both in terms of the shift of the 650-nm line and rate of increase of the normalized photoluminescence intensity. In all cases the photoluminescence from the fibers was less than the Raman intensity. No radioluminescence was observed in either fiber. The radiation resistant fiber exhibited photobleaching effects on the Raman transmission when photoannealed with 488-nm laser light.**

I. Introduction

THE effect of nuclear ionizing radiation on optical fibers is of concern in a variety of applications. For example, some applications of fiber optic chemical sensors involve deployment in a low-to-moderate radiation environment [1]. Raman scattering fiber optic chemical sensors typically utilize excitation wavelengths that are visible and are at shorter wavelengths due to the increased Raman scattering cross section within this spectral band. There has been much work done on the optical properties of optical fibers exposed to nuclear ionizing radiation. However, much of this work has been concerned with wavelengths in the near IR and with radiation dose rates greater than 1 krad(Si)/hour. This work addresses the optical response of irradiated silica fibers that are visible to near IR at dose rates less than 1 krad/hour.

Raman scattering is weak compared to other chemical analytical spectroscopic techniques such as IR absorption and fluorescence. The feasibility of fiber optic Raman scattering chemical detection depends on good fiber transmission and the absence of a strong interference signal from the fiber. The detection of chemicals in a nuclear radiation environment with a Raman fiber optic chemical sensor may be impeded by strong background interferences such as radioluminescence [2] or radiation damage-induced photoluminescence [3], from the optical fiber. Radiation damage in the optical fiber will also decrease the transmission of the Raman scattered light through the fiber. Compounding this effect is the reduction in transmission of the excitation light.

Since the Raman scattering signal is proportional to the inverse fourth power of the exciting light wavelength, it is generally preferable to perform Raman measurements with visible instead of near IR excitation. However, the decreased Raman scattering cross section at longer wavelengths may be compensated by the lower radiation induced fiber transmission loss.

Manuscript received April 8, 1994; revised September 19, 1994.

The authors are with Naval Research Laboratory, Washington, DC 20375-5000 USA.

IEEE Log Number 9407275.

II. Experiment

Two commercial multimode silica fibers were provided by Hanford-Westinghouse for testing, one a communications grade fiber (Corning Inc. 50/125 CPC3) with no radiation hardening treatment, and the other a nominally radiation-resistant step index fiber (Polymicro FIP200220240) with a polyimide buffer coating [4]. Both the Corning and the Polymicro fiber have a pure silica core with OH^- content of less than 2-ppm and a fluorosilicate cladding. The samples were between 50 and 60 meters in length, coiled around a two-inch diameter hollow paper cylinder with approximately 9 meter pigtails for the laser input and output ends. The fibers were continuously irradiated with a ^{60}Co source at a constant dose rate of between 500 and 900 rads/hour.

In situ photoluminescence and Raman measurements were performed in a forward scattering geometry while the fibers were being irradiated. The laser excitation wavelengths employed were 488-nm and 514.5-nm from an Argon Ion laser and 830-nm from a laser diode. For the 488-nm excitation measurements, a scanning spectrometer and GaAs photomultiplier detector were used as discussed previously [4]. The 514.5-nm and 830-nm excitation measurements were performed with a SPEX 270M spectrometer and SPEX Spectrum One CCD detector. Of the two types of optical fibers tested, the main parameters that were altered were the dose rate and excitation wavelength. Table I summarizes the test conditions.

TABLE I

Fiber #	Fiber	Fiber Length (meters)	Dose Rate (rads/hour)	Excitation Wavelength (nm)
1	Corning 50/125 CPC3	60	880	488
2	Polymicro FIP200220240	60	880	488
3	Polymicro FIP200220240	51	560	514.5
4	Polymicro FIP200220240	50	560	830

The fibers were continuously illuminated with laser light as they were being exposed to gamma irradiation. The laser light power was held constant for periods of several hours and then changed to investigate the relationship of photobleaching [4] with incident laser power for those silica fiber measurements performed with 488- and 514.5-nm excitation. The laser light power was held constant throughout the measurements with 830-nm excitation.

III. Results and Discussion

A. Raman

Typical Raman and photoluminescence spectra of the fibers before and during irradiation are shown in Fig. 1. Fig. 1(a) and 1(b) exhibit spectra for 488-nm excitation while 1(c) and 1(d) exhibit spectra for 514.5-nm excitation. The intensity of the Raman spectra have been normalized to account for the different laser power input into the fibers during an irradiation period. However, the initial absolute Raman intensity of the Polymicro fiber was 10% less than the Corning fiber for 488-nm excitation. In this case the laser excitation power and the fiber lengths were the same. The Raman features between 400 cm^{-1} and 1300 cm^{-1} are fundamental Raman features. Weaker overtone Raman bands can be seen between 1500 cm^{-1} and 2500 cm^{-1}. The assignment of these Raman features has been discussed previously [4]. The OH stretch Raman line at 3700 cm^{-1} was not large enough to be detected with the scanning spectrometer—GaAs PMT system, but is evident with the larger signal to noise fixed grating—CCD detection system.

The strength of the Raman signal normalized to the incident laser power steadily decays as the fiber is being irradiated due to the darkening of the fiber. Notice that for the Polymicro fiber the Raman spectra out to 2000 cm^{-1} retains nearly the same shape with irradiation. This implies that the attenuation in the fiber induced by radiation damage is nearly the same throughout this wavelength region (515–575-nm). The intensity of the strongest Raman line as a function of total radiation dose is shown in Figs. 2 and 3 for the four irradiated fibers. The Raman intensity is normalized to the pre-irradiation Raman intensity. Different regions of the Raman intensity versus total dose curves in Figs. 2 and 3 were fit to exponential decay curves, $I = I_0[\exp(-d/d_0)]$, where I_0 is the initial Raman intensity, d is the accumulated radiation dose, and d_0 is an exponential decay constant to be determined. The Corning fiber with 488-nm excitation displayed the largest Raman intensity decrease with irradiation. The initial irradiation decay constant for the Corning fiber was 4.4 krads. The Polymicro fiber displayed a greater radiation resistance with 488-nm excitation compared to the Corning fiber as evidenced by a larger Raman decay constant of

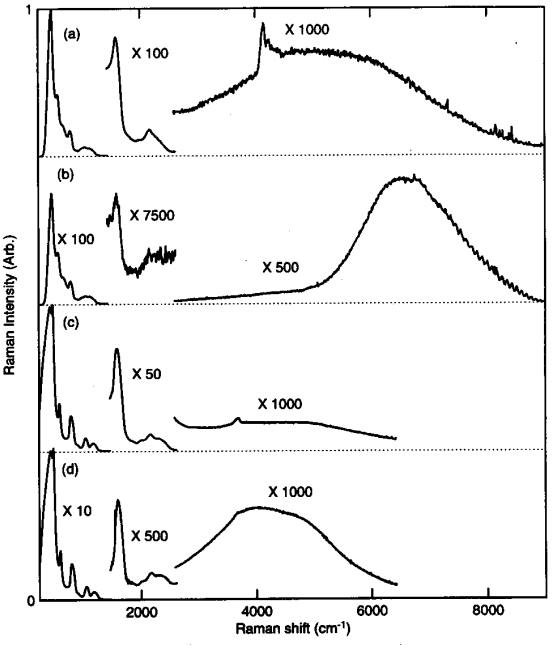

Fig. 1. Typical Raman spectra of irradiated silica fiber. (a) Corning fiber, 488-nm exc., 0.0 krads. (b) Corning fiber, 488-nm exc., 45.5 krads. (c) Polymicro fiber, 514.5-nm exc., 0.0 krads. (d) Polymicro fiber, 514.5-nm exc., 66.3 krads.

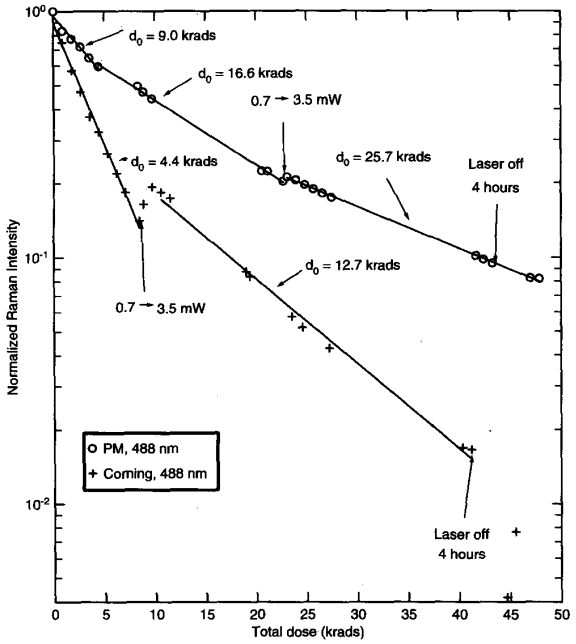

Fig. 2. Raman intensity of Polymicro and Corning silica fiber versus accumulated radiation dose with 488-nm excitation.

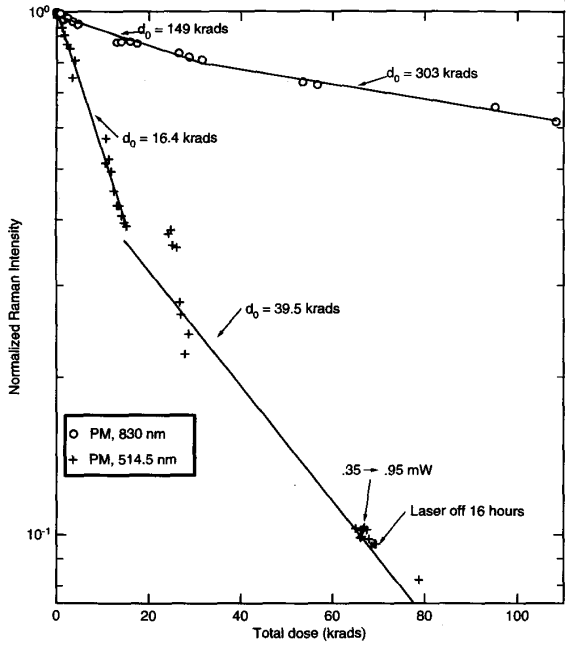

Fig. 3. Raman intensity of Polymicro silica fiber versus accumulated radiation dose with 514.5-nm and 830-nm excitation.

9.0 krads initially. The radiation resistance of the Polymicro fiber at 514.5-nm excitation is only 15% better than at 488-nm when the difference in sample fiber lengths is taken into account. The radiation resistance is much better at 830-nm than at the shorter wavelengths as seen in Figs. 2 and 3.

The Raman signal decay curves in Figs. 2 and 3 were smooth for the most part, except at the points where the laser light power coupled into the fiber changed. The exception to this was the Raman signal decay curve of the Polymicro fiber with 514.5-nm excitation. There is an anomalous hump in the curve around 25–30 krads. The origin of this behavior is unknown.

The decay constant decreased with irradiation dose for all the fibers studied as seen in Figs. 2 and 3. One explanation for this behavior is that a fraction of the radiation activated defect or defects responsible for the attenuation in the Raman transmission may be more susceptible to activation through irradiation. Once the number of these activated defects saturates, the decay constant will necessarily decrease.

Since the radiation dose rate and lengths of fiber exposed is different for the fibers studied, we cannot directly compare the Raman transmission decay curves of Figs. 2 and 3. However, one may use the decay constant results from these curves to calculate the Raman transmission decay for a standard length of fiber and dose rate assuming that the radiation damage of the fiber is linear with dose rate over the range in this study (550–800 rads/hour). For typical conditions expected in the nuclear waste tanks, approximately 20 meters of fiber will be exposed to 100–1000 rads/hour. The point at which the Raman transmission of a fiber optic probe is sufficiently degraded to warrant replacing is somewhat arbitrary. However, a degradation to 30% of the original Raman transmission is significant. Table II lists the time for 20 meters of fiber exposed to 550 rads/hour to drop to 30% of the original fiber Raman signal. The time value for 830-nm excitation distinguished by an asterisk was extrapolated from our data. The Polymicro fiber lasts more than three times as long when 830-nm excitation is utilized when compared with 488-nm or 514.5-nm excitation. The increased degradation of the Raman transmission with a decrease in laser excitation wavelength from 830-nm to 488-nm is consistent with the increase in optical attenuation as the wavelength decreases over this optical range [5].

The previous discussion of the most appropriate laser excitation wavelength does not take into account, however, the increased Raman scattering at shorter wavelengths. Assuming that the laser excitation power is the same for all wavelengths and that the fibers must remain in the waste tanks for a period of three months or more, 830-nm excitation is still the most appropriate for use with a Raman probe.

Photobleaching of the radiation-induced Raman attenuation is evident for the Corning fiber in Fig. 2. Here it is evident that the Raman intensity begins to increase for a few hours after the laser input power is increased from 0.7 to 3.5 mW. At the higher laser input power the irradiation decay constant increases, indicative of the greater photobleaching rate of the radiation induced Raman attenuation.

The Polymicro fiber with 488-nm or 514.5-nm excitation was much less susceptible to photobleaching of the defect center responsible for the Raman attenuation during radiation compared to the Corning fiber. However, the light power density was greater in the Corning fiber since the fiber core diameter was 50 microns as compared to 200 microns for the Polymicro fiber.

TABLE II

Sample	Excitation Wavelength (nm)	30% Raman Intensity (450 cm^{-1} Raman line)
Corning 50/125 CPC3 communications fiber	488	2.9 days
Polymicro FIP200220240 low OH silica fiber	488	6.2 days
Polymicro FIP200220240 low OH silica fiber	514.5	7.1 days
Polymicro FIP200220240 low OH silica fiber	830	24.2 days*

20 meters of fiber exposed. 550 rads/hour dose rate.

A post irradiation photoanneal was performed on Polymicro fiber #3. After a total accumulated exposure of 77.9 krads fiber #3 was no longer exposed to gamma irradiation. 15-mW of laser light power at 488-nm was then injected into the fiber for a period of 48 hours. The fiber transmission for 514.5-nm excitation recovered from 7.6% to 13.1% of the original fiber Raman transmission indicating that the defect responsible for the radiation induced transmission loss may be photoannealed with visible light.

IV. Photoluminescence

In addition to the Raman features in Fig. 1 there is a broad photoluminescence line at 650-nm (Raman shift of 5100 cm^{-1} and 4050 cm^{-1} for 488-nm and 514.5-nm respectively). This photoluminescence feature has been associated with an absorption at 630-nm and attributed to the nonbridging oxygen hole center (NBOHC) [6], [7].

This NBOHC defect is intrinsically present in many silica fibers and has been shown to be dependent upon the fiber drawing process [8] which creates drawing induced nonbridging oxygen hole centers (DINBOHC). Additionally, the NBOHC may be introduced through high energy irradiation of silica glass forming radiation induced nonbridging oxygen hole centers (RINBOHC) [6], [7].

A photoluminescence line at 540-nm has been observed by others for an excitation wavelength of 458-nm in both all silica and hydrogen enriched silica fibers and attributed to E' center creation [9]. There was no evidence of this 540-nm luminescence line in either fiber for the excitation wavelength of 488-nm. Radioluminescence with no exciting laser light has also been observed at 650-nm for silica fiber under x-ray stimulation [2]. No radioluminescence was observed in our study.

For comparison of the photoluminescence features in the fibers, the intensities of the features have been normalized to the strength of the 450 cm^{-1} Raman line as shown in Fig. 4. The shift in the position of the luminescence peak upon irradiation of the Corning fiber indicates that the origin of the photoluminescence due to drawing induced defect centers and radiation induced defect centers may be different. This behavior has been noted by others [9] in silica fibers. The apparent long wavelength shift of the 650-nm photoluminescence might also be explained by an increased attenuation in the fiber at wavelengths on the high energy side of the luminescence peak. This explanation is consistent with the 630-nm absorption induced in silica fibers under irradiation. There was no shift in the position of the luminescence of the Polymicro fiber under irradiation.

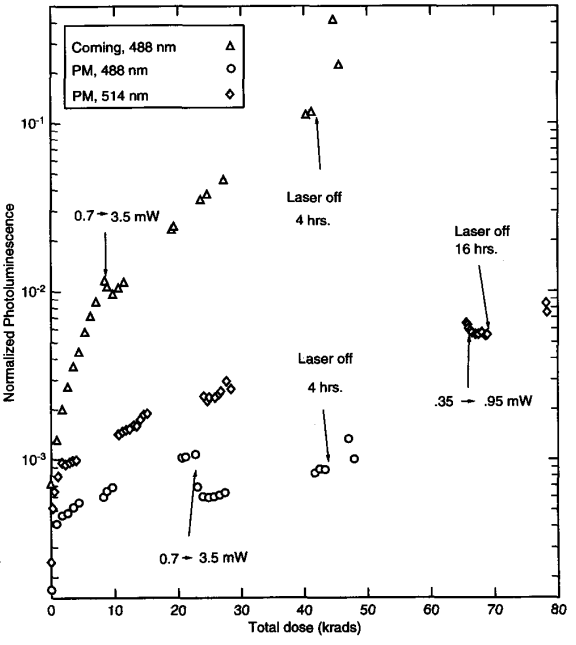

Fig. 4. Photoluminescence intensity normalized to 450 cm^{-1} Raman line intensity versus accumulated radiation dose.

The normalized intensity of the photoluminescence peak of the Polymicro fiber initially increases strongly upon irradiation but then flattens out after the first few hours. The normalized photoluminescence intensity of the Corning fiber continued to increase throughout the irradiation and no saturation was evident. As seen in Fig. 4, the 650-nm luminescence is reduced in both the Corning and Polymicro fibers by photobleaching with 488-nm light. Upon increasing the intensity of the incident laser light coupled into the fiber from 0.7- to 3.5-mW the normalized photoluminescence decreases initially. After a couple of hours the photoluminescence begins to increase again.

Although increasing the laser intensity coupled into the fiber from 0.7- to 3.5-mW decreases the photoluminescence, the photobleaching is incomplete. A fiber input laser power of 3.5-mW is insufficient to overcome the damage due to the *in situ* irradiation. The light intensity in the fiber is not the same throughout because of transmission loss. Therefore, although the regions of the fiber closer to the input end may be receiving light power strong enough to photobleach the 650-nm photoluminescence, regions of the fiber near the output end are receiving substantially less and will photobleach at a slower rate.

V. Conclusion

The results of an *in situ* Raman and photoluminescence study of two silica fibers, one nominally radiation resistant, exposed to low to moderate gamma irradiation levels has been presented here. The rate of decrease of the silica fiber Raman signal with gamma irradiation is much less in the radiation-resistant fiber compared to the commercial communications fiber for 488-nm laser excitation (see Fig. 2). The Raman attenuation of the radiation resistant fiber with radiation exposure is more than three times greater for 488-nm or 514.5-nm excitation compared to 830-nm excitation. The Raman attenuation of the silica fibers can be photoannealed slightly with 488-nm laser light. Photoannealing with 15-mW of 488-nm laser light for a period of 48 hours increased the fiber Raman transmission in the Polymicro fiber from 7.6% to 13.1% of the original Raman transmission.

A Raman fiber optic chemical sensor will have sufficient Raman transmission degradation to warrant replacing the fiber at an arbitrary value of 30% of the pre-irradiated transmission. In typical radiation exposure conditions found in nuclear waste tanks (550 rads/hour, 20 meters fiber length exposed) the Polymicro low OH fiber would require replacing at 24.2 days, and 7.1 days for 830-nm and 514.5-nm excitation, respectively. Near-infrared excitation is recommended for this fiber. Currently, studies of the effect of radiation on the Raman transmission of a high OH radiation resistant Polymicro fiber are underway.

No radioluminescence was detected in the fibers studied. The photoluminescence at 650-nm does not pose problems in these fibers for applications as part of a fiber optic probe. At the radiation dose level where the photoluminescence intensity approaches the fiber Raman intensity the low transmission of the fiber would render the fibers unacceptable as part of a fiber optic Raman probe.

References

[1] R. Greenwell, R. S. Addleman, B. A. Crawford, S. J. Mech, and G. L. Troyer, presented at the DOD 3rd Biennial Fiber Optics Conference, 1992.

[2] M. J. Marrone, "Radiation-induced luminescence in silica core fibers," *Appl. Phys. Lett.*, vol. 38, no. 3, pp. 115–117, 1981.

[3] S. R. Ediriweera and F. Kvasnik, "Optical fibre radiation damage measurements," *Optical Systems in Adverse Environments, SPIE*, vol. 1399, pp. 64–75, 1990.

[4] T. G. Bilodeau, K. J. Ewing, G. M. Nau, M. Gingerich, E. J. Friebele, I. D. Aggarwal, F. Reich, and S. Mech, "In-situ Raman and photoluminescence of gamma irradiated silica fibers," in *SPIE Optical Sensing for Environmental Monitoring*, vol. 2068, 1994.

[5] E. J. Friebele, G. H. Sigel Jr., and M. E. Gingerich, "Radiation response of fiber optic waveguides in the 0.4 to 1.7 micron region," *IEEE Trans. Nucl. Sci.*, vol. NS-25, no. 6, pp. 1261–1266, 1978.

[6] J. W. H. Schreurs, "Study of some trapped hole centers in x-irradiated alkali silicate glasses," *J. Chem. Phys.*, vol. 47, pp. 818–830, 1967.

[7] D. L. Griscom, "Nature of defects and defect generation in optical glasses," *Radiation Effects in Optical Materials, SPIE*, vol. 541, pp. 38–59, 1985.

[8] P. Kaiser, "Drawing-induced coloration on vitreous silica fibers," *J. Opt. Soc. Am.*, vol. 64, no. 4, pp. 475–481, 1974.

[9] S. R. Ediriweera and F. Kvasnik, "Spectral measurements in gamma irradiated optical fibres using attenuation and Raman spectroscopy," *Fiber-Optic Metrology and Standards, SPIE*, vol. 1504, pp. 110–117, 1991.