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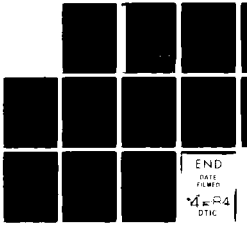

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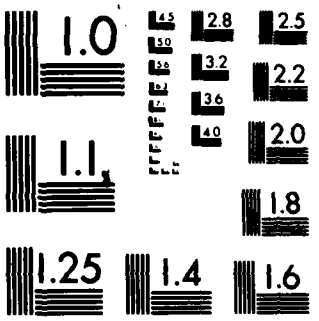

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A STUDY OF THE MECHANICS OF RADIATION DAMAGE IN FIBER OPTICAL WAVEGUIDES

Final Report

G. R. Blair

MARCH 1984

U.S. ARMY RESEARCH OFFICE

CONTRACT NO. DAAG29-80-C-0139

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20. ABSTRACT (Continue on reverse side if necessary and identify by block number)

Ionizing radiation on optical fibers induces large transmission losses. The permanence and intensity of the damage depends on the concentration of germanium and phosphorus. The sensitive structure(s) may act as electron or hole traps when illuminated with gamma rays (1.2 meV) or ultraviolet (4.9 eV). The process of emptying traps by heat and refilling with UV (254 nm) can be done repeatedly. These traps re-populated by UV are the same as the transmission loss traps due to gammas. Certain TL traps cannot be re-populated with UV. The nonrefillable TL traps exist in those glasses which have the

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GeO_2/P_2O_5 ratios smaller than 4. Higher ratio glasses exhibit one refillable peak which bears an inverse relationship to germanium content. The TL traps have a depth of about 0.85 eV. Pure silica fibers display a permanent thermoluminescence. The presence of these traps is not detected by transmission measurements. Based on UV thermoluminescence, transmission, and UV fluorescence measurements, it is suggested that Ge^{+2} plays an important role in the damage mechanism.

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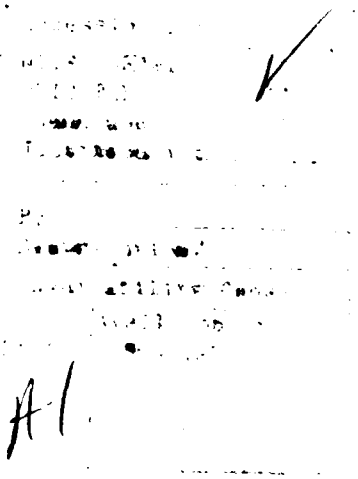

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INTRODUCTION

When optical fibers are used in an ionizing radiation field, the IR transmission quality is degraded, depending on the dose and the rate at which they are irradiated. The research conducted during this contract (#DAAG-29-80-C-0139) has been directed toward an understanding of the mechanisms of the generation of defects which absorb the transmitted light signal.

This research has depended on three basic measurements for the collection of data:

- Transmission, either fixed at 0.8 μm, or spectral from 350 nm to 1200 nm.
- Thermoluminescence
- Ultraviolet fluorescence.

The source of gamma radiation was ^{60}Co. Late in the program we found that ultraviolet light below 350 nm served equally well to fill the traps responsible for transmission loss.

Fibers studied on this program have all been fabricated by the MCVD process and drawn at Hughes Research Laboratories (HRL). This has given us a great advantage in altering composition of the fibers.

Griscom and Friebele[1] have presented a rather complete review of the absorbing species in pure and doped silica, as found by Electron Spin Resonance studies. In pure silica these workers have identified the following defects:

- The E' center
- The peroxy radical
- The non-bridging oxygen hole center.

In doped silica glasses Griscom et al. have identified the following defects:

- Boron-oxygen hole center (and the equivalent [Al]° defect)
- E' centers due to germanium, boron, and/or phosphorus
- A series of defects due to phosphorus, labeled as P_1, P_2, P_4, POHC.

These defects have been found in the glasses saturated by the ionizing radiation. The research on this program, has been directed toward the effects of rather low doses (3×10^4 rads) on doped silica fibers since it is in such fields that the bulk of communication fibers will be used. It is because of the low dose and high glass complexity that our data do not always agree with those obtained from saturation studies. It is interesting that Griscom points out that at low doses ($\leq 10^5$ rads) a different E' center is formed of which little is known except that it differs dramatically from the high dose ($> 10^6$ rads) E'center.

EXPERIMENTAL PROCEDURES

The radiation source used in our work is a company facility at Fullerton, California. This unit is a "Canadian Atomic" system and employs twelve pellets which may be used independently or synchronously. The dose rate may be varied continuously if desired, and the sample is irradiated from 360° rather than a single point source. It was highly adaptable to fiber use since the measurement equipment could be placed next to the shielding of the source, was readily accessible and uniformity of irradiation was assured. Much of the transmission data were collected in situ during the irradiation.

Transmission measurement equipment consisted of two separate units:

- A pulsed LED system operating at 0.8 μm
- A spectral unit operating at 0.35 μ to 0.85 μm, or 0.7 μm to 1.4 μm.

The spectral unit (see Figure 1) employed a 100 W quartz-iodine lamp as a source. The transmitted light from the fiber was chopped and fed to an Oriel 0.25 m monochromator. The detector was an RCA 4832 photo multiplier tube, using a GaAs cathode.

The thermoluminescence (TL) unit was a Harshaw 2000 TL detector. The temperature sensor for the planchett was modified to ensure repeatability of the temperature ramp. This unit was not spectrally selective, other than incorporating a blue/filter to remove IR. A special TL head was constructed to attach to the Oriel monochromator for spectral TL measurements, and used the temperature ramp of the Harshaw unit.

The studies on re-population with UV (to be described) employed a Bausch & Lomb monchromator or a very narrow band pass filter for obtaining the illuminating light.

The UV source for all irradiations was a Pen-ray lamp with quartz envelope. The lamp puts out 4400 μW in the short wave region. Approximately 90% of the output in that region is at 254 nm, so that for all practical purposes, the 254 nm line has an approximate intensity of 0.004 W.

The data from the Oriel spectrometer are collected by a computer as well as being drawn on an x-y plotter. The computer then automatically calculates such functions as dB/Km, absorbance, normalization, and derivitives. This sophistication in data manipulation was incorporated late in the program.

Preforms were produced by the MOCVD process, using $SiCl_4$, $GeCl_4$ and/or $POCl_3$ as glass formers. Other dopants such as Ni or Ce were introduced through a gas-seal on the gas handling mechanism. The rate of introduction of Ni or Ce depends on the vapor pressure of the compounds which is controlled by a heater. The quantities of gas for depositing the glass were controlled by a Tylan gas handling system, also arranged for computer

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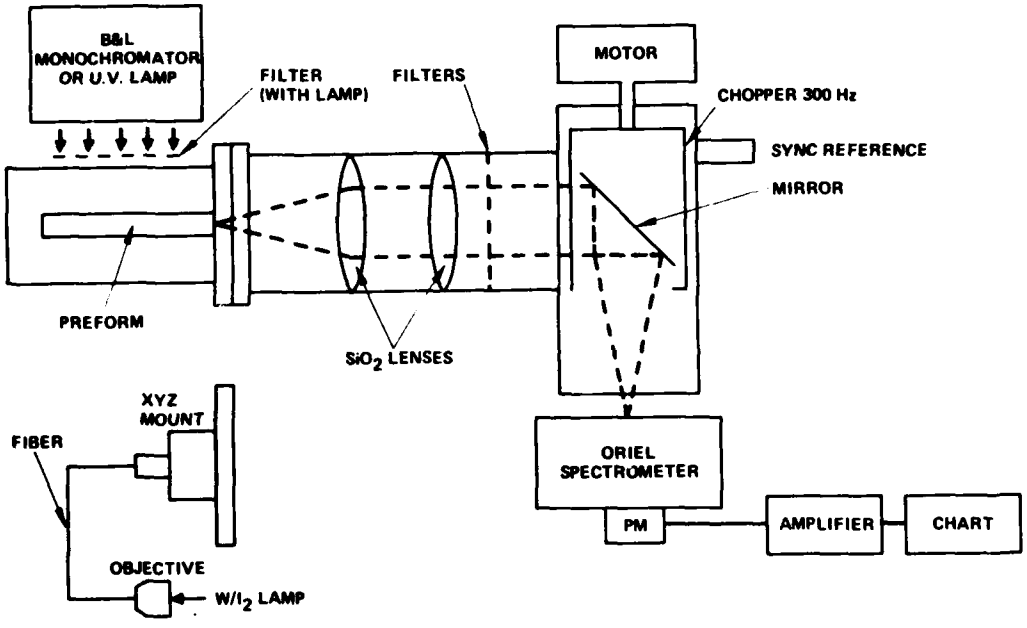

Figure 1. Apparatus for measuring UV emission of preforms and spectral transmission of fibers.

control. Temperature control of the preform tube was through the Tylan system fed from an IRtran pyrometer operating at two frequencies in the 5 to 7 μ range. Preforms so generated were drawn to fiber from an Astro furnace shielded by N_2. The fiber was jacketed with aluminum in-line from a molten source. Only about one kilometer of fiber was drawn from each preform.

DISCUSSION

Composition

The compositions of the various fibers have been determined in two ways:

- EDAX on the core of the fiber
- Spectrography on the excess preform fluff (core glass).

The majority of analyses have been obtained by the EDAX technique. This has presented certain standardization problems and interferences which compromised the analysis. We consequently began using the excess fluff from the preform tube as the sample, to represent only the core glass. The glass fluff is analyzed by arc emission spectrography with much better accuracy and sensitivity than can be obtained by the EDAX technique, also sample preparation is much easier. We have also tried the technique described by Bell Labs wherein the SiO_2 is volatilized as SiF_4. This process turned out to be bulky, time consuming, prone to contamination, and tends to lose constituents other than only SiO_2, so that the accuracy is compromised. The arc emission spectrography eliminates any measurement of preform or fiber dimension, which would be required, for the volatilization technique back calculations. A table of preforms from which fibers were drawn for study is presented as Table 1.

Table 1. Analysis of Fibers Decreasing GeO_2 Mol %

Number		GeO_2	GeO_2/P_2O_5	P_2O_5
V-47		22.5	∞	0
V-43		19.7	∞	0
V-42		16.0	8.4	1.9
V-10		14.8	74.0	0.2
P1-19-8		14.2	2.5	5.6
P-86		11.0	1.4	8.0
V-28		8.0	∞	0
V-29		7.9	4.6	1.7
V-11		7.9	26.3	0.3
V-27 (No Fiber)		7.8	4.9	1.6
V-31 (No Fiber)		7.8	3.9	2.0
V-7		7.1	3.2	2.2
P-67		6.5	1.6	4.0
P-10-8-8		6.4	2.3	2.8
V-8		6.03	50.0	0.12
V-26 (Flat)		4.8	3.4	1.4
V-25		4.75	3.5	1.35
P-83		4.2	21.0	0.2
V-9		1.5	4.5	0.33
P-84		1.4	0.2	6.8
V-18		1.06	∞	0
V-20		0.95	0.41	2.3
V-21		0.8	0.32	2.5
P-66		0.68	0.76	0.9
P-63		0	0	4.5
V-19		0	0	2.1
V-50		14.65	∞	0
V-53		9.81		0
	SiO_2			
V-17	100	0		0
V-23	100	0		0

Transmission Loss

A typical transmission loss plot at 0.82 μm is shown in Figure 2. The linear relationship of dB/km vs. dose applies to all the phosphorus-containing fibers studied. These data agree with Griscom et al.[3] in which is it is pointed out that the phosphorus-related defect centers are thermally stable, and that the population grows linearly, independent of dose rate at least up to 10^6 rads.

Spectral transmission curves are shown in Figure 3 as obtained. The exceedingly strong absorption is clearly evident up to about 700 nm. The data are presented in Figure 4 in conventional absorbance vs. wavelength form.

Transmission measurements were coupled with annealing experiments following gamma or UV illumination. For the germanium-phosphorus fibers studied, a common annealing pattern was obtained. This is shown in Figure 4 in conventional absorbance vs. wavelength form. The shift in absorption edge is seen easily as one moves along the visible tail of the intense E' absorption. Also, the complete emptying of the traps responsible for 700 to 800 nm absorption is visible as the dramatic drop in residual induced loss after 600°C heating.

The structure(s) which are responsible for the transmission traps are not destroyed even at 800°C. This was shown by re-populating the same traps which had been filled by gamma dose and emptied by heat (as shown by the same spectral transmission) with ultra-violet light (< 350 nm). This re-population is shown in Figure 5. In this experiment, a coil of fiber 10 m long was stripped of the aluminum jacket. The spectral transmission was measured before and after the irradiation in situ. The coil was then heated in steps, obtaining the spectral transmission at room temperature after each step. The coil was then illuminated by the UV and the spectral transmission was again measured. The re-population is quite evident, as indicated by curve 5. It does not reproduce curve 2, from γ, due to intensity effects

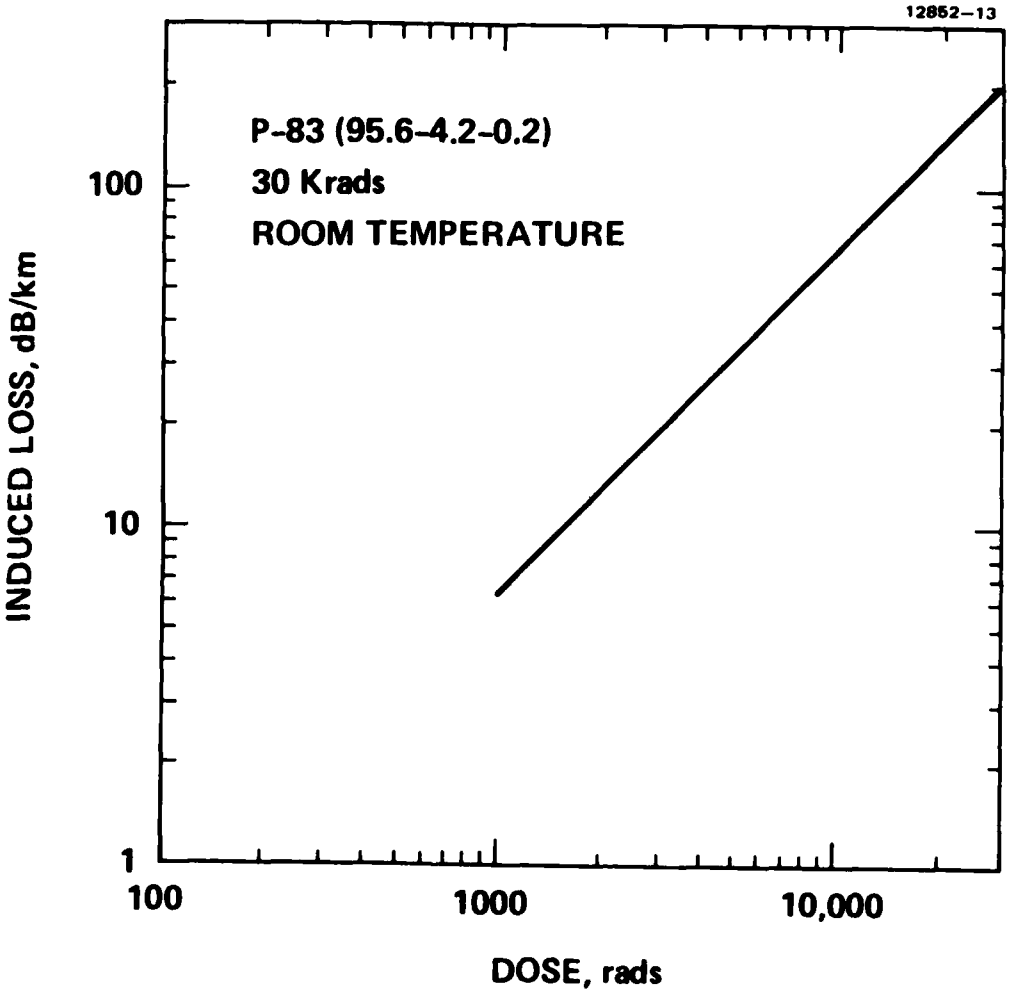

Figure 2. Typical in situ induced loss vs dose.

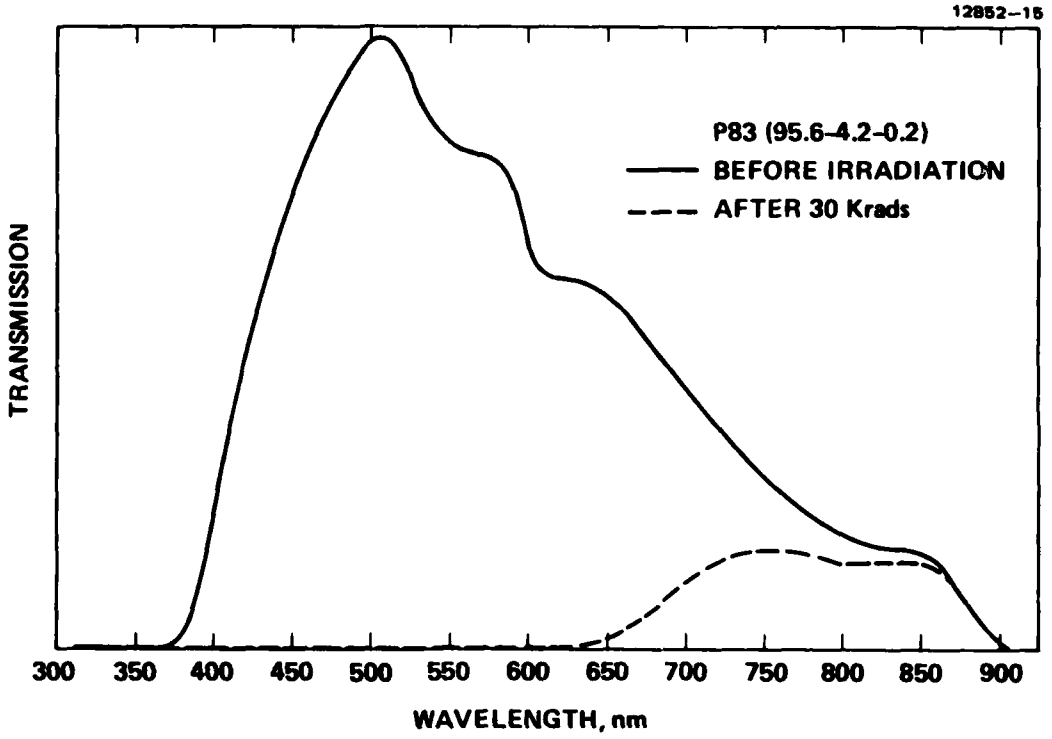

Figure 3. Radiation induced changes in spectral transmission.

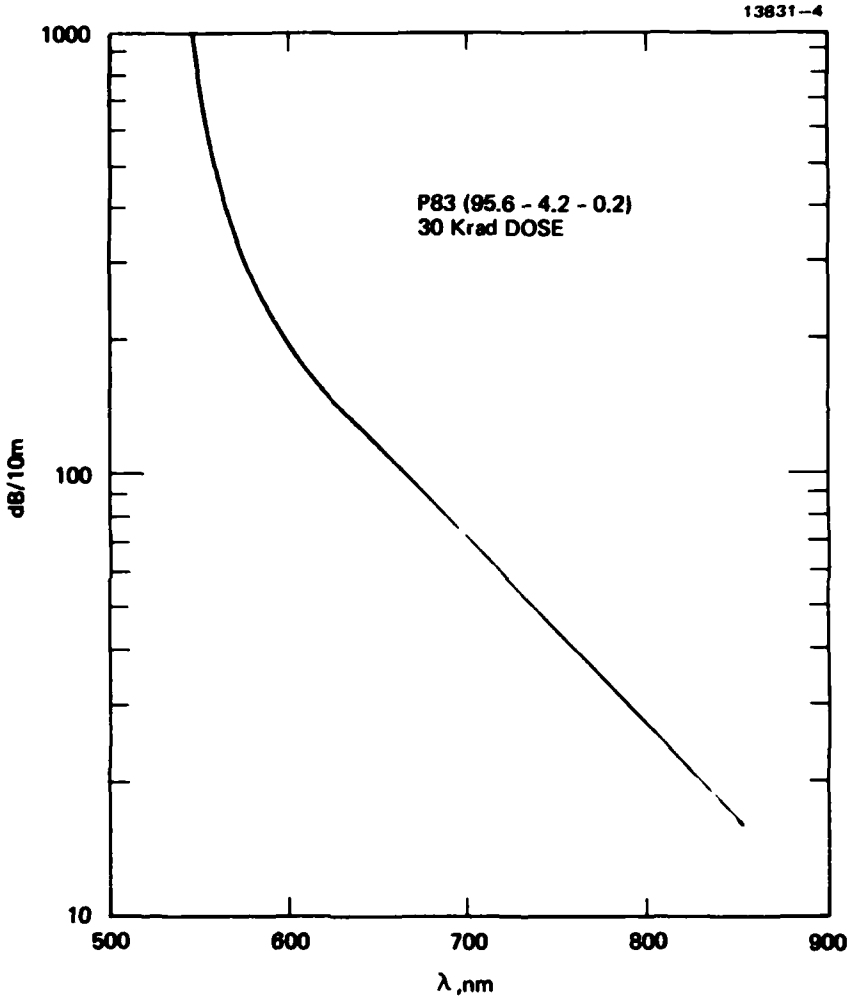

Figure 4. Radiation induced transmission vs wavelength.

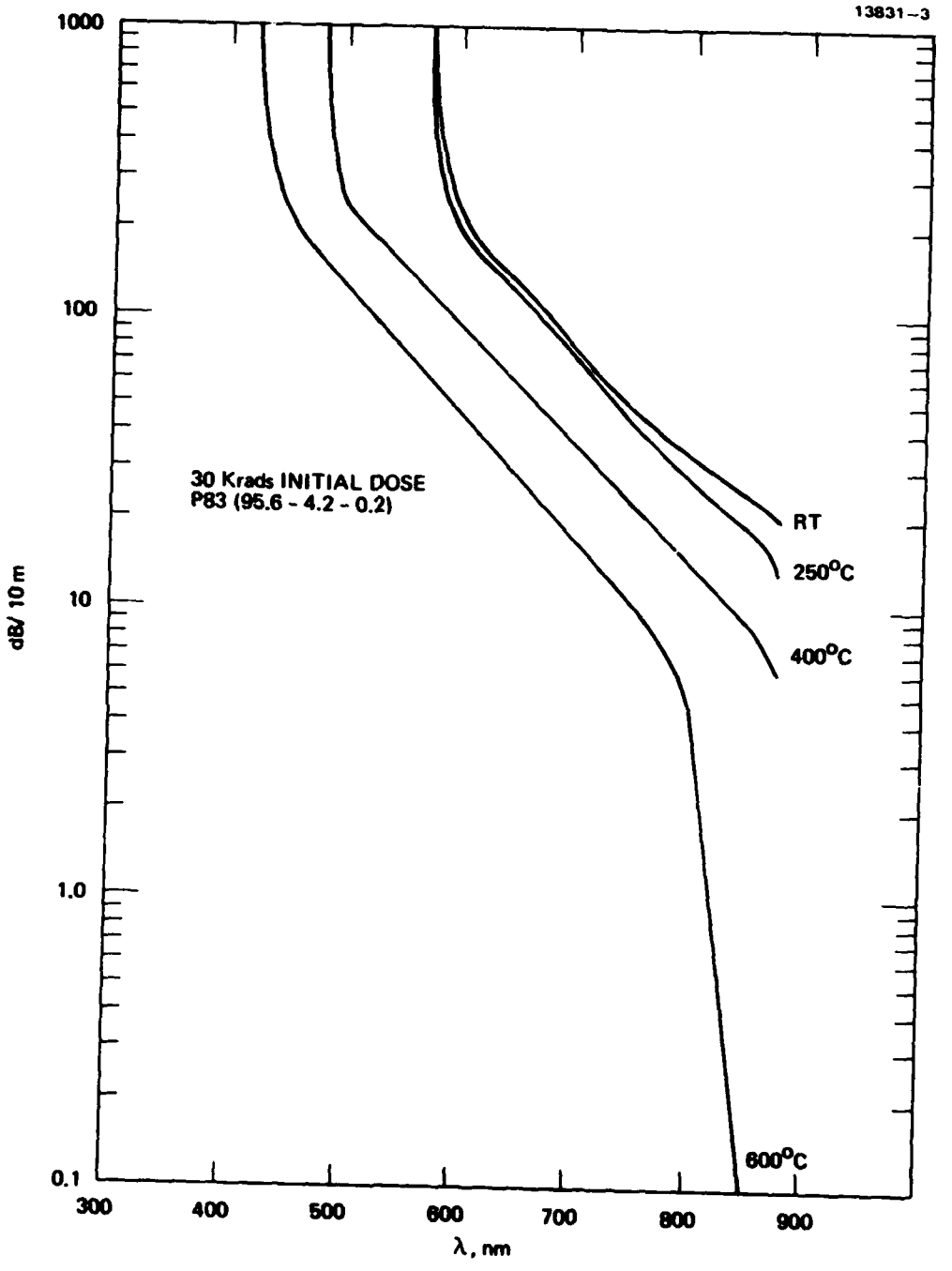

Figure 5. Induced loss after heating.

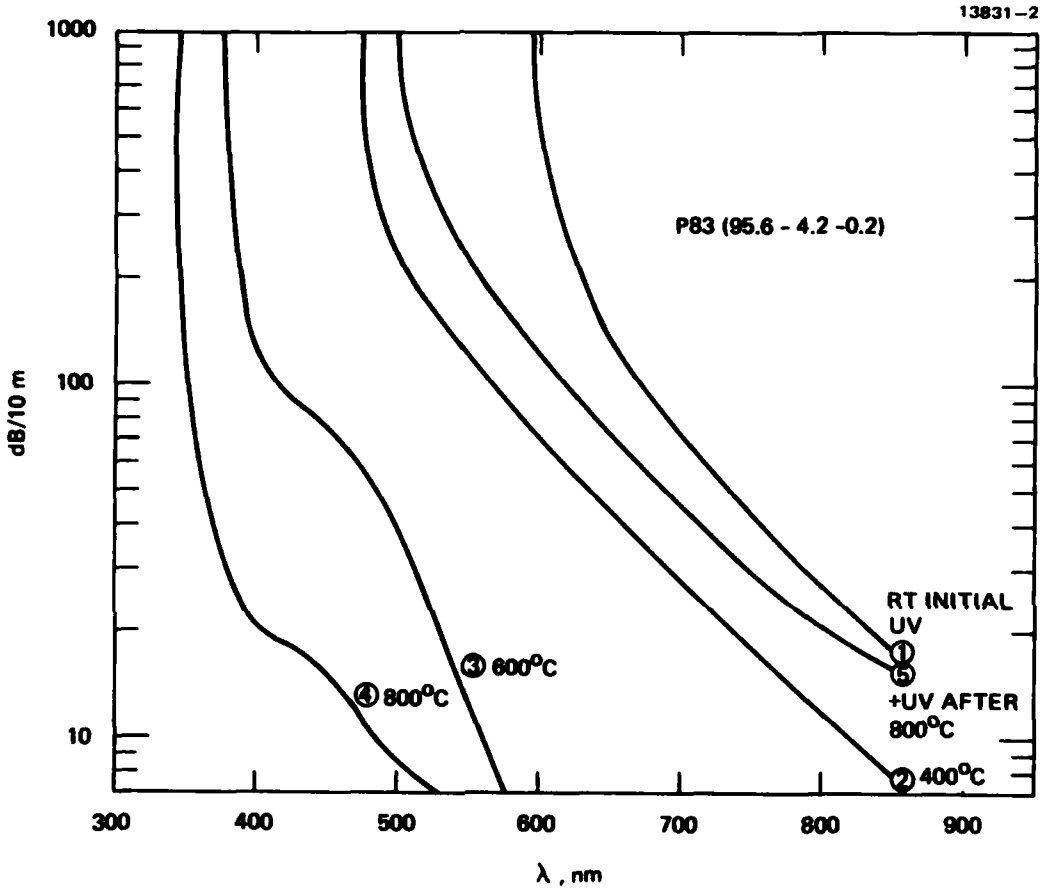

Figure 6. Annealing of induced loss due to UV at RT as function of temperature.

between UV and γ. Moreover, the same traps may be filled by UV in pristine fiber which has never been subjected to radiation. This indicates that much of the trap structure is intrinsic to the drawn fiber, and that the defect sites need not necessarily be generated by the 1-mev gamma rays rupturing bonds. This is shown in Figure 7 by the intensification of the absorption bands with time of illumination (compare with Figure 3).

The traps filled by the UV are also annealed in the same fashion as if the filling had occurred under gamma irradiation. The fact that the transmission traps may be filled by UV and annealed out in the same way indicates that the traps are identical for γ filling or UV filling.

UV Fluorescence

In addition to filling the transmission loss traps, the UV radiation also excites fluorescence in fibers. The fluorescence is remarkably single valued, being exclusively in a very narrow band centered at 400 nm. The intensity is dependent on the germanium and phosphorus content. After 30 K rads, the UV fluorescence intensity is degraded in those fibers which contain phosphorus. We have shown that the fluorsecence is excited solely by the 254-line of the mercury lamp.

Since the fluorescence is due only to the 254 nm light, we feel confident that the emitted light is due to the Ge^{+2} absorption at 245 nm.

Thermoluminescence

A rather large part of our effort has been devoted to using thermoluminescence (TL) as a diagnostic tool. Most samples have been powdered, although a few tests were conducted with fibers. We have favored the powder sample because of the reproducibility factor. It was found early in the program that the cleaving of fiber ends was highly unreproducible, so that the intensity measurments suffered during comparison of runs. Also, the signal from the core glass, which is, after all, the item of interest, was found to be many times that from the silica jacketing,

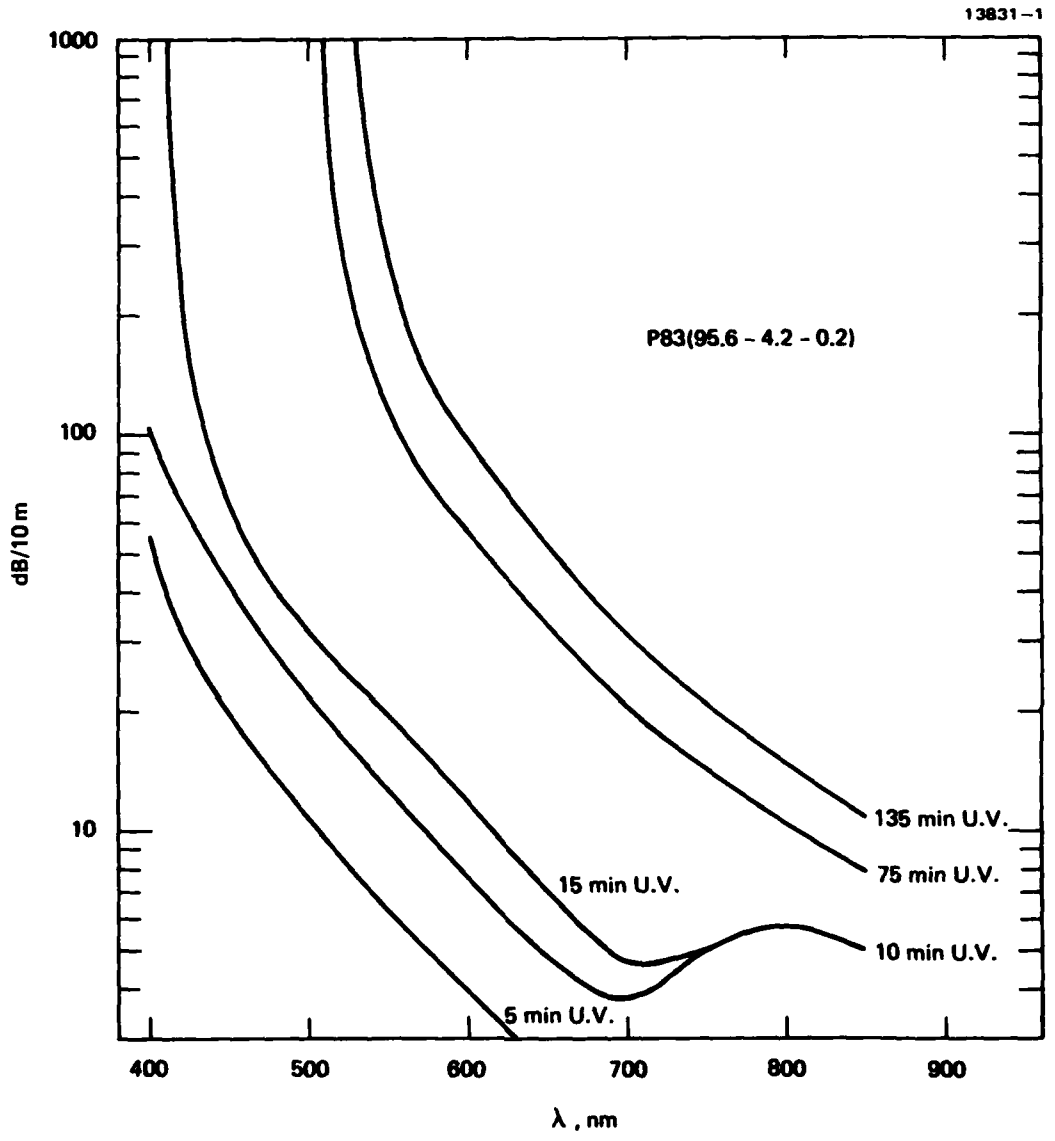

Figure 7. Induced loss vs wavelength at various doses of UV on Pristine fiber.

even though the silica used for the MCVD tube (Hereaus TO-8) had some impurities in it and consequently some undefined background thermoluminescence. The background is presumably due to the natural germanium content of the Hereaus tubing.

The TL from the Si-Ge-P fibers is highly dependent on the composition, and also on mechanical factors such as drawing force and drawing temperature. We have now accumulated sufficient data which show that after a 30 K-rad dose of gammas the ratio of GeO_2/P_2O_5 controls whether the TL emission is from two or one trap depth. However, the emission detected is invariably in the range of 450 to 500 nm. This would imply that there is a single recombination site through which all the electrons must pass. As shown in Table 2, when the GeO_2/P_2O_5 ratio is greater than 4 (preponderance of germanium over phosphorus) the TL emission is single peaked with the maximum temperature around 290°C. When the ratio is less than 4 (preponderance of phosphorus over germanium) there are always two peaks observed, one at about 160°C and the other at around 375°. The two-peak TL emission tends to duplicate the pure SiO_2 emission peak location, but is modified in intensity by the phosphorus and/or germanium content.

The TL Curve for a pure SiO_2 core fiber has two well defined, but broad, peaks, one at ~ 160°C and the other at about 380°C. The intensity is almost one order of magnitude lower than that for a fiber which has a low germanium content. The addition of phosphorus to this pure system generates a new peak at about 260°C, and reduces the high temperature peak. When the phosphorus exceeds the germanium by about 4 times, the TL mimics that for pure SiO_2-P_2O_5 glass, but is about 1/2 the intensity of that from pure SiO_2.

A phenomena which is currently being examined involves the core cladding (sometimes referred to as a barrier layer). In this system the single-double peak pattern is avoided, if the cladding is Si-F rather than Si-P. The data are shown in

Table 2. Correlation of TL Emission with GeO_2/P_2O_5 Ratio

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SAMPLE NO.	GeO_2	P_2O_5	RATIO	SINGLE	DOUBLE
V-10	14.8	0.2	74.0	X	
V-8	6.0	0.12	50.0	X	
V-11	7.9	0.3	26.0	X	
P-83	4.2	0.2	21.0	X	
V-9	1.5	0.3	5.0	X	
P-86	11.0	8.0	1.4		X
P-66	0.68	0.9	0.76		X
V-20	0.95	2.3	0.4		X
V-21	0.8	2.5	0.3		X
P-84	1.4	6.8	0.2		X
V-19	0	2.1	0		X
HRL100 (SiO_2)	0	0	0		X

Figure 8. Here the two separate peaks are readily observed. It should be pointed out that the 160°C peak intensity is dependent on the germanium content. The 380°C peak is dependent on the phosphorus/germanium content. The effect of phosphorus alone is shown for V-19 and the difference curve, showing the 260°C peak that is characteristic of high germanium-phosphorus fibers. The single broad peak shown by the fibers with Si-P cladding (Figure 8) may in actuality be an envelope of three peaks, the two at 160°C and 350°C being highly attenuated and the one at 260°C being intensely accentuated (presumeably due to some reaction of phosphorus with the germanium). That any TL could be detected from the pure silica core fiber was surprising since transmission measurements show that the permanent induced loss was neglible or within the error of measurments. The TL data, however, show that there are some traps permanently filled in the pure silica which are not annealed at room temperature and not necessarily observed by transmission.

The data of Table 2 indicate that a significant change occurs in the structure of the doped silica glass, depending on the GeO_2/P_2O_5 ratio. When the ratio is > 4 the waveguide resembles a Si-Ge glass in its behavior. If the P_2O_5 predominates (ratio < 4), the glass behaves as a silica-phosphorus one and the double peak system results.

The intensity of the single peak system is dependent on the germanium content. This is shown in Figure 9 after 30K rads of gamma. Higher concentration of germanium reduces the TL emission intensity, similar to a concentration quenching as observed in UV fluorescence of the SiO_2-GeO_2 system. The base emission for pure SiO_2 has been subtracted from the curves of Figure 9. These fibers all had a Si-P barrier layer deposited before the core glass.

We have shown that when phosphorus predominates over germanium it reduces the TL emission, in some cases, below that for pure silica. Since the TL emission is mostly from the

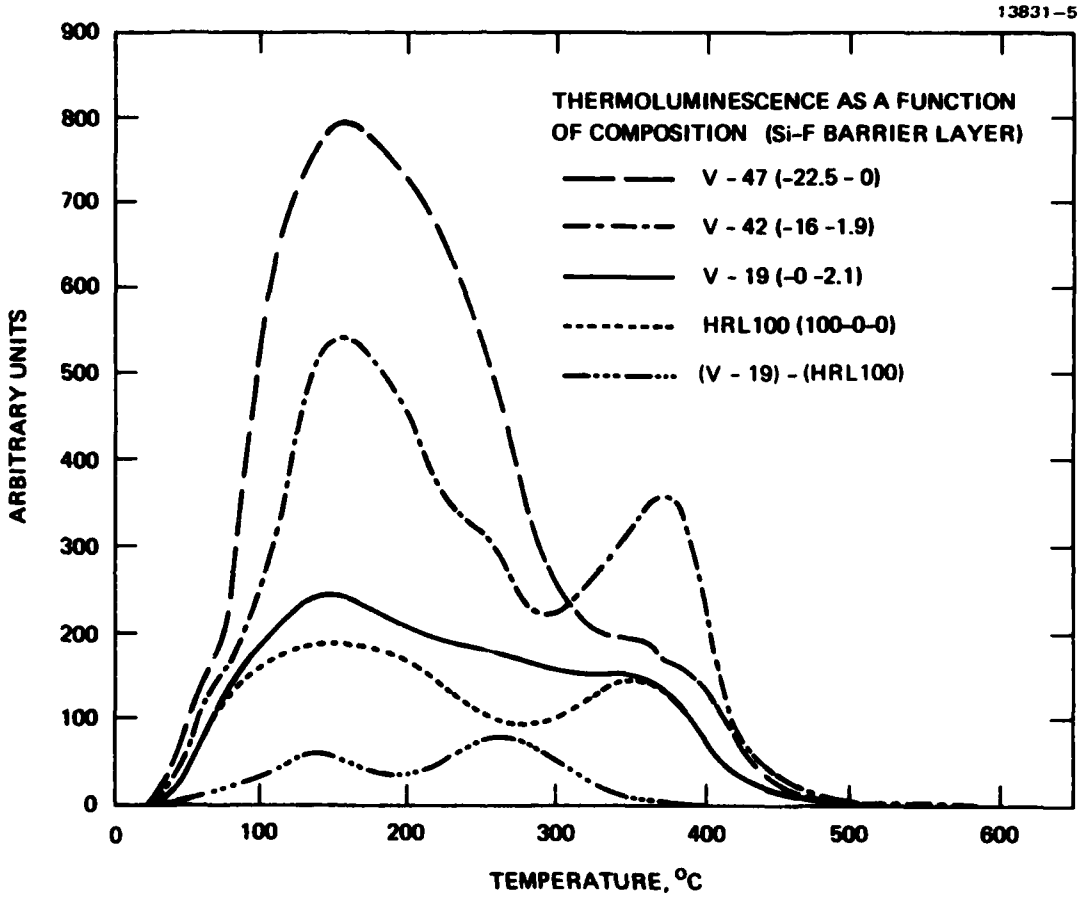


Figure 8. Thermoluminescence as a function of composition.

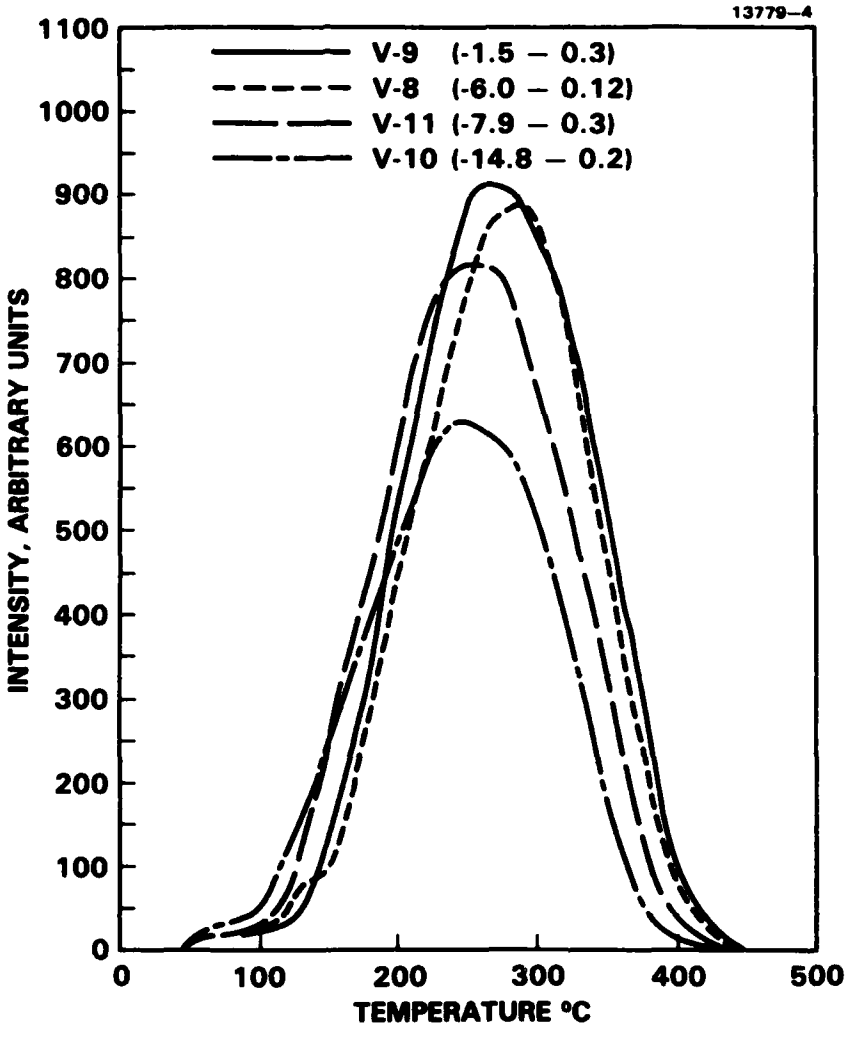


Figure 9. Thermoluminescense as a function of Germunium content.

germanium (at least it is observed with much higher intensity in fibers containing germanium), we take this to mean that somehow the thermally emissive structure due to germanium is greatly affected by the phosphorus. Since we know that the UV fluorescence is also reduced by the phosphorus and is due to the Ge^{+2} content, it is apparent that the phosphorus must then alter the structural relationships existing between the silica lattice (solvent) and the germanium (solute). If one assumes that the germanium is deposited in the silica as Ge^{+4} at relatively low temperatures, then at a temperature of about 2300°C, experienced during shrink down, the equilibrium,

$$GeO_2 \rightleftarrows GeO + \frac{1}{2} O_2 \quad , \qquad (1)$$

is shifted to the right. The germanium that originally was incorporated easily in the silica lattice as Ge^{+4} now occupies a silica site as Ge^{+2}, and would then act as a divalent glass modifier. This would then easily generate defect sites, which would be susceptible to alteration by ionizing radiation. One may further suggest that the oxygen released by the shift of Equation (1) to the right could destroy some of the silica E' precursors, reducing its effect, as well as generating the peroxy bond from the E' precursor structure.

The TL emission may then be due to the defect center created by the Ge^{+2} rather than the Si center. This is most certainly the case for the UV fluorescence.

We have shown that the traps filled by gammas and responsible for the TL two-peak system are of distinct, different types. One trap (about 160°C) is re-populated by UV with wavelengths shorter than 350 nm (we believe it to be only 254 nm). The other trap (about 370°C) is not able to be re-populated by the UV. The refillable traps may be emptied by heating to 600°C, and re-populated with the UV many times, whereas the high temperature traps are never re-populated. This is shown in

Figure 10. The 370°C trap is not re-populated, as shown at (a). Moreover the result does not depend on composition, as shown in (b).

It should be noted here that the transmission traps (described earlier) may be repeatedly re-populated by UV in the same manner as for the TL.

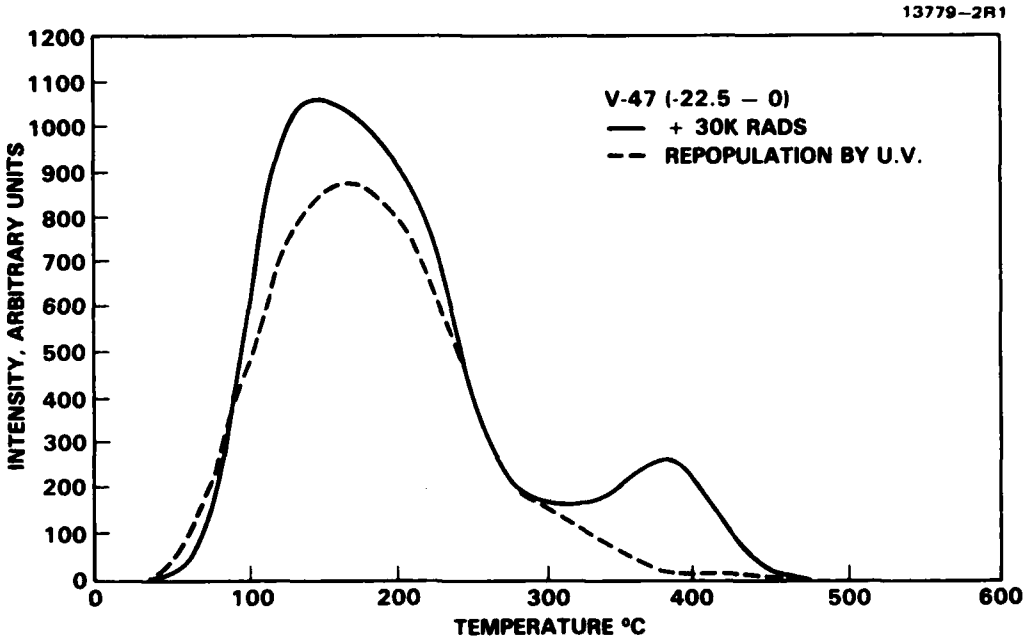
It is known that traps which are excited by UV are populated by electrons, and not holes. This leads us to believe that the TL traps and transmission traps re-populated by UV are electron traps. These are the 150°C and 280°C TL traps. Because the 370°C traps are not filled by UV we believe they are hole traps. The depth of the traps depends on a complex relationship between germanium and phophorus in the silica lattice. Since we have not correlated any TL with ESR data we cannot assign actual structures (i.e., the P_1, P_2, P_4, and POHC, as defined by Griscom).

We have determined by the procedure of Van Gorkum, that the TL emission is second order in kinetics; i.e., that the retrapping and recombination probabilities are equal.

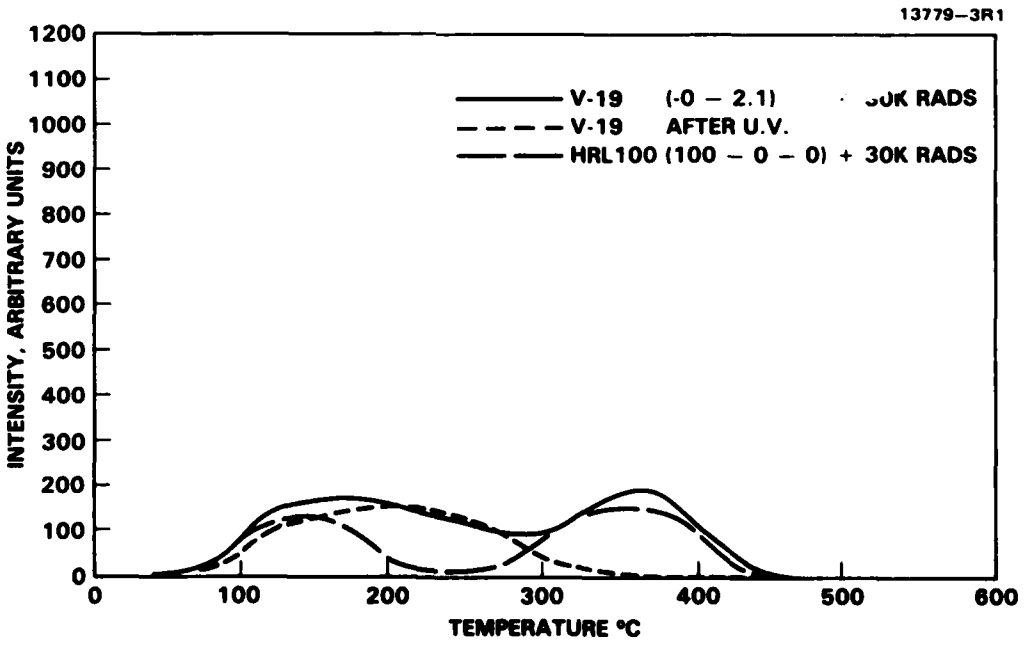
SUMMARY

We have shown that the optical absorption traps in optical fiber glasses tend to anneal somewhat at room temperature, whereas the TL traps do not.

TL intensity and pattern has been shown to be related to the GeO_2/P_2O_5 ratio. At low ratios (where the phosphorus predominates), two distinct peaks are found which mimic the two peak TL structure of pure SiO_2. When germanium predominates (high ratio) there is only one peak observed. We have correlated this effect with UV fluorescence. In this case the "germanium" glasses (high ratio) yield a high intensity fluorescence peak. In "phosphorus" glasses (low ratio) the UV fluroescence is low. These effects may be related to the alteration of the Ge^{+2} content of the glasses by the phosphorus which acts as a quencher.



(a)



(b)

Figure 10. Re-population of TL traps by UV.

The kinetics of TL have been shown by an analysis using van Gorkum's techniques to be second order. The depth of the traps varies from about 0.8 ev to 1.1 ev.

On the basis of UV re-population experiments described above, we assigned the 150°C and 260°C peaks to be due to electron traps and the 380°C peak to be due to a hole trap.

The TL emission is found to be almost exclusively in the 450 to 470 nm spectral region. This holds for all the compositions of glass that we have examined. We conclude then, that although the TL traps may have several thermal depths, the recombination site is a single one, to which all the electrons migrate.

We have also shown that the defects in drawn fiber are inherent and may be filled by either UV (< 35 nm) or gamma rays. This indicates that the inherent defects are due to dangling oxygens, Si-Si bonds or highly strained Si-O bonds.

REFERENCES

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