

Neutron Specific Color Center in Fused Silica and an Impurity Band of Identical Wavelength*

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A color center at 242 $m\mu$ is produced in certain specimens of fused silica only by pile irradiation and not by x-ray, high energy electron, or proton bombardment. It is removed by heating to 700°C and can be reintroduced only by pile irradiation. The significance of an impurity absorption band already reported in fused silica at the same wavelength is discussed. An intense band appears in rather pure optical-quality fused germanium dioxide centered at 245 $m\mu$ and is due to the same reduced germanium species that causes the 242- $m\mu$ impurity band in fused silica.

I. INTRODUCTION

THAT fused silica developed a weak band at 242 $m\mu$ upon reactor exposure was earlier reported by Levy¹ for a specimen of Corning "purified" fused silica. At the same time it was shown by Cohen² that x-irradiation of the Corning material does not produce this band. Nelson and Crawford³ found that fast neutrons also introduce a poorly resolved band at 275 $m\mu$ in Corning silica. These workers suppose their band to be the same as that found by Levy at 242 $m\mu$. The 242 $m\mu$ band discussed here is probably that one of the B_2 bands of Mitchell and Paige⁴ which is located at 5.2 eV (238 $m\mu$) in neutron-irradiated optical quality fused silica obtained from the Thermal Syndicate. These workers found the B_2 bands to increase with neutron dosage, the maximum dosage being 7×10^{17} neutrons/cm².

An understanding of this color center at 242 $m\mu$ is complicated by the presence of an impurity band at the same wavelength, which is present or can be developed in most fused silica. Several of the reports on this impurity band are not in harmony. It is unaffected by x-irradiation and annealing at 700°C. Yokota⁵ attributes this band to interstitial silicon atoms and was the first to point out that the intensity of the fluorescence in fused silica becomes larger as the band is enhanced by heating the silica under reducing conditions. Garino-Canina⁶ at first attributed the 242- $m\mu$ band to a metallic impurity present in the silica and found three luminescent emission bands at 280, 396, and 436 $m\mu$. The latter band is produced by reducing treatment of the silica. He associates the luminescent centers with metallic impurity present in the glass.⁷

In a later experiment⁸ he removed the 242- $m\mu$ absorption band and the ability of the fused silica to luminesce by electrolysis at 1000°C. Garino-Canina⁹ was able to reintroduce the 242 $m\mu$ band and luminescence by heat treatment of this silica under reducing conditions. He then concludes, in concordance with Yokota, that the centers responsible for the 242 $m\mu$ band are interstitial silicon atoms. On the contrary, Cohen² has shown that the 242 $m\mu$ band cannot be produced in some samples of fused silica upon comparable reducing treatment and concludes, in accord with Garino-Canina's earlier belief,⁶ that the 242 $m\mu$ band is associated with an impurity. Dainton and Rowbottom¹⁰ suggest the possibility that the thermoluminescence in fused silica (incidentally containing the 242 $m\mu$ band) is due to lead impurity. They find that the ratios of lead contents and of thermoluminescence intensities are nearly the same for two different silica specimens.

Since the experimental portion of this paper has been completed, Garino-Canina has published unequivocal proof¹¹ that the 242 $m\mu$ impurity band is due to germanium. This is shown by production of the band in varying degrees in fused silicas matching addition of varying amounts of this impurity. He has thus revised his interpretation⁹ that the band is associated with interstitial silicon. The results of the present work and of Garino-Canina now mutually confirm the fact that the 242 $m\mu$ band is due to germanium impurity in a reduced state.

II. EXPERIMENTAL

The three sets of specimens of fused silica used in this investigation were a series of wafers of Heraeus fused silica known as Homogenized Ultrasil grade,¹² a series of wafers of Corning purified fused silica, uv grade,¹³ with $k=0.800$ cm⁻¹ (74% transmission for 1.5-mm thickness) at 186 $m\mu$, and a series of special

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† Multiple Fellowship on Glass Science.

¹ P. W. Levy, J. Chem. Phys. **23**, 764 (1955).

² A. J. Cohen, J. Chem. Phys. **23**, 765 (1955).

³ C. M. Nelson and J. H. Crawford, Jr., Bull. Am. Phys. Soc. Ser. II, 1, 214 (1956).

⁴ E. W. J. Mitchell and E. G. S. Paige, Proc. Phys. Soc. (London) **B67**, 262 (1954).

⁵ R. Yokota, J. Phys. Soc. Japan **7**, 316 (1952).

⁶ V. Garino-Canina, Compt. rend. **238**, 1577 (1954).

⁷ V. Garino-Canina, Compt. rend. **239**, 875 (1954).

⁸ V. Garino-Canina, Compt. rend. **240**, 1331 (1955).

⁹ V. Garino-Canina, Compt. rend. **240**, 1765 (1955).

¹⁰ F. S. Dainton and J. Rowbottom, Trans. Faraday Soc. **50**, 480 (1954).

¹¹ V. Garino-Canina, Compt. rend. **242**, 1982 (1956).

¹² Purchased from the Amersil Company, Inc., Hillside, New Jersey.

¹³ Purchased from Corning Glass Works, Corning, New York.

samples of Corning purified fused silica with $k=0.163$ cm^{-1} at $186\text{ m}\mu$ (76% transmission for 0.80-cm thickness).

Absorption spectral data were taken on a Beckman Model DU Spectrophotometer having a photomultiplier attachment. Air was used as a standard. The data presented are not corrected for background or reflection.

The x-ray irradiations were made in a Picker Industrial Unit with a Machlett AEG 50T tube with tungsten target and beryllium window. The irradiations were at 50 pkv, 20 ma, 6 cm from the tube window. The dosage rate is in the order of 1.5×10^6 r/hour in air at the surface of the specimen. The irradiations were carried out near room temperature (34°C). All samples were wrapped in aluminum foil before the irradiation and transferred to the spectrophotometer in subdued light to eliminate light bleaching of the color centers under study. The samples were all protected from light during storage at room temperature.

The Ultrasil and Corning fused silicas subject to pile irradiation were placed in Rabbit 2 of the Brookhaven pile where the flux is 3.1×10^{12} slow neutrons/sec cm^2 and the fast neutron flux is one-third of this amount. The sample temperatures while in the pile were 70°C or less.

The proton bombardment was performed in the Saxonburg Cyclotron of the Carnegie Institute of Technology. The samples received 3.8×10^{15} protons/ cm^2 at 400 Mev. The irradiations given an Ultrasil and Corning sample were the same within $\pm 10\%$.

The electron-bombarded Ultrasil received 1.25×10^8 reps (roentgen equivalent physical units) of 2-Mev electrons from a Van de Graaff generator. (The actual flux value was not available.) It was protected from light with aluminum foil.

III. RESULTS AND DISCUSSION

A. Impurity Band at $242\text{ m}\mu$

As stated earlier,² this band could be produced in Ultrasil grade Heraeus fused silica which did not originally contain this band, by heat treatment at 1000 to 1400°C for 2.5 hr using sugar carbon, silicon, or silicon carbide powders. The intensity of the band was independent of the type of reducing agent used but dependent on temperature to 1300°C . Treatment at 1400°C gave no enhancement over 1300°C . The data obtained were not precise enough for heat of formation calculations. The Corning purified silica treated under identical conditions at 1400°C did not develop the $242\text{-m}\mu$ band. Table I gives a comparison of impurities in Heraeus Ultrasil and the Corning silica with $k=0.800$ cm^{-1} at $186\text{ m}\mu$.

These analyses were made on powdered samples and on trace residues remaining after removal of the silica by treatment with hydrofluoric acid in platinum ware. The impurities reported from residues are only those which were not found in blanks run on the same

quantity of hydrofluoric acid as used for dissolution of the glass.

Since beryllium and germanium were found in Ultrasil but not in Corning silica, these elements were regarded as possible sources of the $242\text{-m}\mu$ band in Ultrasil. Germanium was chosen first for investigation because of its easy reduction and the established existence of a lower valence state. In addition, the ultraviolet absorption spectrum of gaseous GeO exhibits absorption lines in the region 2261 to 2478 \AA .¹⁴

Because of the difficulty of producing a high purity fused silica containing uniformly dispersed germanium impurity, it was decided to investigate first the absorption spectrum of a rather pure optical quality germanium dioxide glass to see if it contained a $242\text{-m}\mu$ peak or if this peak could be produced by mild reducing treatment. Earlier workers found an ultraviolet cutoff at $315\text{ m}\mu$,¹⁵ and at around $280\text{ m}\mu$ ¹⁶ for a 2.51-mm thick sample of high purity fused germanium dioxide.

In this laboratory, optical quality high-purity fused GeO_2 ¹⁷ free of bubbles was prepared and thin polished wafers were made in order to study the ultraviolet region below the lower reported cutoff. (A detailed account on GeO_2 glass will be transmitted later.) In a $72\text{-}\mu$ thick wafer, the optical density was 1.940 at $272.5\text{ m}\mu$. By use of fine copper screens as a reference, it was possible to extend the optical density range of the Beckman Spectrophotometer to almost four with decreased precision. A $100\text{-}\mu$ thick polished wafer gave the spectrum shown in Fig. 1. An absorption maximum was found at $245\text{ m}\mu$ with $k=3.6 \times 10^2$ cm^{-1} . It appears that another peak may be present below $222\text{ m}\mu$ which was the cutoff when this method was used. An emission analysis of this material showed the following impurities (in ppm)¹⁸: Ca, present; Cr, 10; Cu, present; Fe, present; Pb, 10; Mg, <10; Mn, 10; Ag, 3; and Si, ~ 100 . The starting material was of higher purity, the

TABLE I. Impurities found by emission analysis in parts per million (ppm).^a

Element	Heraeus Ultrasil	Relative concentration	Corning purified silica
Al	<10	>	<10
Be	trace ^b	>	absent
Ca	>5, <10	=	>5, <10
Cr	>1	=	>1
Cu	>5 (strong)	>	>5 (medium), <10
Fe	<10	=	<10
Ge	trace ^b	>	absent
Mg	<5	=	<5
Na	absent	=	absent

^a Absolute values between $\frac{1}{3}$ and 3 times values indicated.

^b Found in residue only.

¹⁴ G. Drummond and R. F. Barrow, Proc. Phys. Soc. (London) **A65**, 277 (1952).

¹⁵ R. W. Shaw, Phys. Rev. **51**, 146 (1937).

¹⁶ N. J. Kreidl and J. R. Hensler, paper VII-3, Fourth International Congress on Glass, Paris, July, 1956 (to be published).

¹⁷ Obtained from Eagle-Picher Company, Miami, Oklahoma as crystalline GeO_2 .

¹⁸ Absolute values between $\frac{1}{3}$ and 3 times values indicated.

major portions of impurity being introduced in production of the glass. An approximate calculation using the Smakula equation gave 135 ppm (assuming an oscillator strength of one) of centers causing the 245 $m\mu$ band. This order of magnitude eliminates detectable impurities other than silicon as being responsible for this band.

It has been shown that the band at 242 $m\mu$ in fused silica cannot be due to silicon.² Therefore it is concluded that this absorption band in fused germania is caused by trace quantities of the same germanium species that produces the 242 $m\mu$ band in fused silica. It appears best to denote this species as either germanium (II) or elemental interstitial germanium. It was planned to produce fused silica from two samples of synthetic quartz containing differing quantities of germanium impurity but this experiment is now unnecessary with publication of the recent work of Garino-Canina.¹¹ As a result of his and the present work there is now no doubt that the 242 $m\mu$ band in fused silica and the approximately 245 $m\mu$ band in fused germania are produced by the same chemical species of germanium. Whether this species is germanium (II) or (0) remains to be determined.

B. 242 $m\mu$ Color Center in Fused Silica

That reactor radiation induced a color center at 242 $m\mu$ seemed confusing at first until it was discovered that this band was indeed a true color center, being partially bleached by ultraviolet light and completely

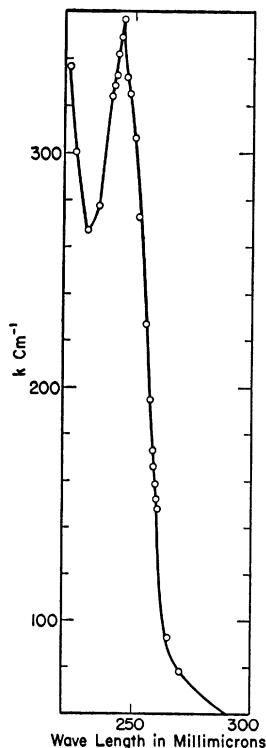


FIG. 1. Ultraviolet absorption spectrum of fused germania wafer of 100 μ thickness.

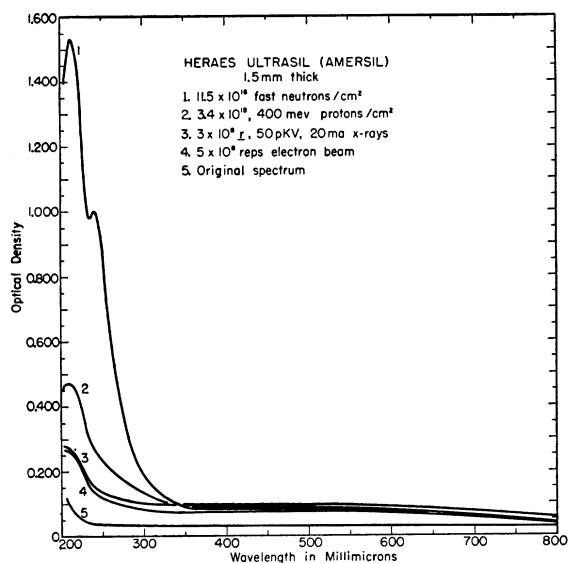


FIG. 2. Comparison of absorption spectra of fused silica before and after various types of high-energy irradiation.

annealed by heating. The center discussed in Sec. A was completely unaffected by heat, ultraviolet light, or more energetic radiations.

As discussed earlier,² Ultrasil (Amersil) develops a 242 $m\mu$ band upon reducing treatment alone. Upon x-irradiation alone, weak color center bands centered at 220, 300, and 540 $m\mu$ appear. These three bands are strongly enhanced upon x-irradiation after reducing treatment. This is due either to increase of the (reduced) cation species required for interaction with the unpaired electron or to an increase in the number of anion vacancies or to both. The production of the 242- $m\mu$ germanium band by reducing treatment could be accompanied by creation of one [if Ge(II) is the product] or two [if Ge(0) is the product] anion vacancies per germanium reduced.

Figure 2 illustrates the effect of four types of radiation upon Ultrasil. Spectrum 1 illustrates a bombardment of 11.5×10^{16} fast neutrons/cm²; in addition the slow-neutron bombardment was three times this value. The well-known 214- $m\mu$ color center appears as well as the subsidiary center at 242 $m\mu$. Proton bombardment with 3.4×10^{15} 400-Mev protons per cm² gave only the 214 $m\mu$ band as shown in spectrum 2. It is not understood why the 242 $m\mu$ band is not found in fused silica after proton bombardment. There are at least two possible explanations for its absence. First, the 242 $m\mu$ band may be more rapidly annealed than the 214 $m\mu$ band by the heat produced during the irradiation. However, estimates suggest that the samples did not go much above 100°C. This should be insufficient to anneal either band unless the centers are much more sensitive to temperature under irradiation than later. Second, the dosage of ionizing radiation is probably larger with the proton irradiation than with the neutron

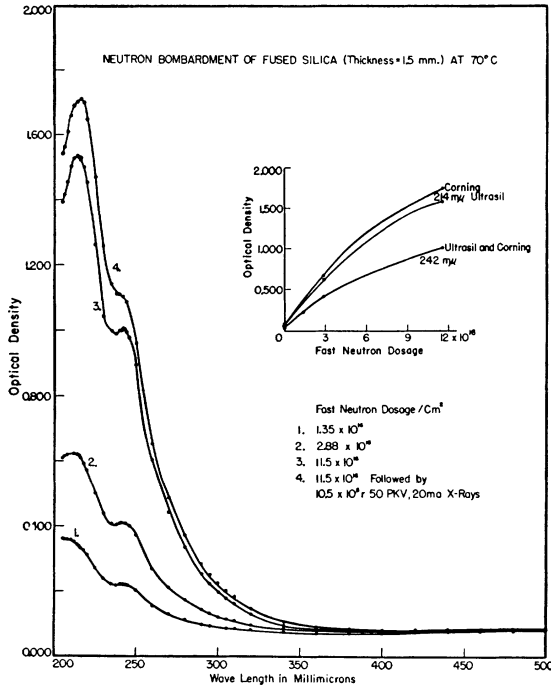


FIG. 3. Absorption spectra of fused silica after reactor irradiation.

irradiation. Since the 214 $m\mu$ band is enhanced by ionizing as well as displacing radiation, the roughly similar heights of the 214 $m\mu$ bands in two of the samples (Spectrum 2, Fig. 2 *vs* spectrum 1, Fig. 3) may not prove that the samples suffered approximate equal numbers of displacements. More prolonged proton bombardments should settle this question. The effect of 3×10^8 r of 50 pkv, 20 ma x-rays is shown in spectrum 3. The 214 $m\mu$ band is ill defined. The effect of 5×10^8 reps (actual flux unavailable) from an electron bombardment is shown in spectrum 4. The results from electron bombardment and x-irradiation are almost identical. Spectrum 5 illustrates the absorption spectrum of the original fused silica without any treatment. The effect of neutron bombardment on the Corning fused silica with $k=0.800$ cm^{-1} at 186 $m\mu$ treated concurrently with the Ultrasil is similar for the 214 and 242- $m\mu$ centers, as will be discussed later. However, this series of Corning samples developed an additional color-center band of very poor resolution located at approximately 260 $m\mu$ under x-ray, electron, and proton bombardment. This band found in no other silica investigated in this laboratory, appears as a distinct peak, and is different from the 242 $m\mu$ band developed in the same material by pile bombardment. The Corning series with $k=0.163$ cm^{-1} at 186 $m\mu$ developed only the 214 $m\mu$ band with x-ray treatment even after a dosage of several billion r. Upon pile bombardment of 11.5×10^{16} fast neutrons, this silica developed the 214 $m\mu$ and 242 $m\mu$ bands. The unique 260 $m\mu$ band is undoubtedly due to impurity contained in the

Corning silica of lower ultraviolet transmission. It is absent in the Corning silica with the higher transparency in the deep ultraviolet and in the Ultrasil studied.

The absorption spectra in Fig. 3 illustrate the effect of three different dosages of neutron bombardment upon Ultrasil. The accompanying Corning silica (analysis Table I) bombarded at the same time gave very similar results. In the plot of optical density *vs* fast-neutron dosage, it is seen that the growth rate of the 214 $m\mu$ band is slightly greater for the Corning material while the rates for the 242 $m\mu$ band are the same in both materials (this neglects any effect on the 242 $m\mu$ band of the slight difference in the optical density of the long-wavelength tail of the 214 $m\mu$ band). The Ultrasil was x-rayed at 50 pkv, 20 ma after pile bombardment. This resulted in apparent growth of both bands as shown in spectrum 4 of Fig. 3. The growth of the 242 $m\mu$ band under x-irradiation however is not a true growth as the increase in the region of this band can be accounted for by the growth of the tail of the 214 $m\mu$ band as taken from data on x-irradiated Corning silica. It has been established that x-ray treatment of Corning silica ($k=0.163$ cm^{-1}) produces only the 214 $m\mu$ color-center band. This follows from the observation that the long-wavelength side of the band is invariant for $\frac{1}{2}k$ during continuing growth to the limit of the spectrophotometer. It is concluded that the band has constant half-width and thus is a simple band.

Results of bleaching studies of Ultrasil are illustrated in Fig. 4. Spectrum 1 shows the sample before bleaching. The bands are both partially bleached by ultraviolet light as shown in spectrum 2. By heating for one hour periods in steps of 50 to 100°C, complete bleaching of both bands was achieved at 700°C as shown in spectrum 3. The bleached Ultrasil was then x-rayed.

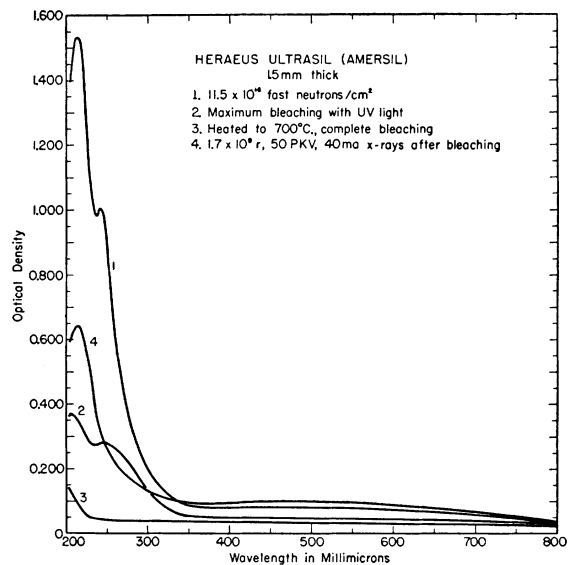


FIG. 4. Reactor-irradiated fused silica bleached by ultraviolet light and then by heat followed by x irradiation.

Spectrum 4 shows that the 242 $m\mu$ band produced by pile bombardment has been annealed out irreversibly and is not produced by ionizing radiation, while the 214 $m\mu$ band appears as is expected but saturates well below the optical density of the band produced by the neutron bombardment. This indicates that this type of center is partially annealed by the bleaching treatment. A cursory investigation of the ultraviolet bleaching of the 214 and 242 $m\mu$ bands in the pile irradiated Ultrasil specimen illustrated in Fig. 4, indicated that the former band decayed at a slightly faster rate. When the 214 $m\mu$ band was about 83% and the 242 $m\mu$ band 76% bleached, no further change occurred. Then the partially optically bleached specimen was heated with little further change until 400°C. At this point the bands were bleached about 91% and 83%, respectively. At 400° they were 95 and 92% bleached and became completely bleached at 700°C.

IV. CONCLUSIONS

The absorption band at 242 $m\mu$ found in most fused silica after reducing treatment results from reduction of germanium impurity present in the glass. This band is independent of the 242- $m\mu$ color-center band produced by pile bombardment. The 242- $m\mu$ color center may be due either to Si(II) or interstitial silicon. Since SiO vapor has a strong absorption band at 2413.8 Å,¹⁹

¹⁹ R. W. B. Pearse and A. G. Gaydon, *The Identification of Molecular Spectra* (John Wiley and Sons, Inc., New York, 1950), second edition revised, p. 224.

the Si(II) is favored. Using the same argument one might favor Ge(II) as being responsible for the 242- $m\mu$ impurity band.¹⁴

This color center shows specificity for fast neutrons. In the present studies it has behaved as a dosimeter over a neutron flux range of 10^{16} to 10^{17} fast neutrons/cm². Further work would be required to establish the limitations of fused silica as a fast neutron dosimeter.

V. ACKNOWLEDGMENTS

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