Effects of a Simulated High-Energy Space Environment on the Ultraviolet Transmittance of Optical Materials between 1050 Å and 3000 Å

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Transmittances of LiF, MgF_2, CaF_2, BaF_2, Al_2O_3, and fused SiO_2 were measured from 1050 Å to 3000 Å before and after irradiation by 10^{14} electrons/cm^2 first at 1.0 MeV and then at 2.0 MeV. Similar measurements were made with 10^{14} electrons/cm^2 at 2.0 MeV using Al_2O_3 to shield fused SiO_2, ADP, calcite, and Corning glass filters 9–54 and 7–54 from the direct electron beam. The electron energy and dose represent what one might expect to encounter in the artificial radiation belt after one year in a circular, near polar orbit at 1400 km. From these measurements it is concluded MgF_2, BaF_2, and Al_2O_3 have the greatest potential for space applications in the uv.

I. Introduction

In recent years there has been considerable interest in the behavior of optical materials in the hostile environment of space. The term *optical degradation* is sometimes used to explain discrepancies between predicted and observed results for space optical experiments. It is the purpose of this work to investigate the effects on transmittance of optical materials for uv use when subjected to irradiation by high energy electrons. The amount of irradiation is determined by what one might expect to encounter for a period of one year in space for a given orbit. This work is restricted to materials which are transparent in the region from 1050 Å to 3000 Å.

It is true that much work has appeared in the literature of solid state physics on the effects of high energy irradiation of optical crystals and glasses. Unfortunately the irradiation dose is usually much larger than what one would expect to encounter in an earth orbit of one year duration. The large doses are used in order to introduce large numbers of crystal defects and color centers. Also, most of the work has been restricted to the nonvacuum region above 2000 Å.

The materials studied in this work were divided into two groups. The first group, composed of LiF, MgF_2, CaF_2, BaF_2, Al_2O_3, and fused SiO_2, was placed directly in the high energy electron beam. The second group composed of fused SiO_2, ADP, calcite, and Corning filters 9–54 and 7–54, was shielded from the direct electron beam by an Al_2O_3 crystal. In the latter, the principal irradiation is the bremsstrahlung resulting from stopping the electrons in the sapphire crystal.

II. Electron Energy Distribution in Space

The Starfish explosion (1.4 Megatons) at 400 km above Johnston Island in July 1962 produced a slowly decaying artificial electron belt. At about 1000 km, the electron energy distribution closely resembled a fission energy spectrum (β-decay from fission fragments).[1] With the passage of time, the energy spectrum is modified by scattering. Calculations by the Laboratory for Theoretical Studies at GSFC show show that by January 1968, 95% of the artificial electrons from Starfish should have energies less than 3 MeV, and 71% less than 1 MeV for a circular, near polar orbit at 1200 km. Thus, it is not unreasonable to simulate the effects of the artificial electron belt by irradiating with electrons at energies in the 1–2-MeV region. For January 1966 in a circular near polar orbit at 1400 km, the predicted maximum flux would be 10^{14} electrons cm^{-2} yr^{-1} if there were no decay.

III. Experimental Procedure

The transmittances were measured at the exit slit of a 1-m McPherson Model 225 monochromator using a Hinteregger-type windowless hydrogen light source. A sample holder was constructed that made it possible either to insert or to remove the crystal from the exit beam without breaking the vacuum.

The crystals listed in Table I were irradiated with 10^{14} electrons/cm^2 at 1.0 MeV and then with 10^{14} elec-

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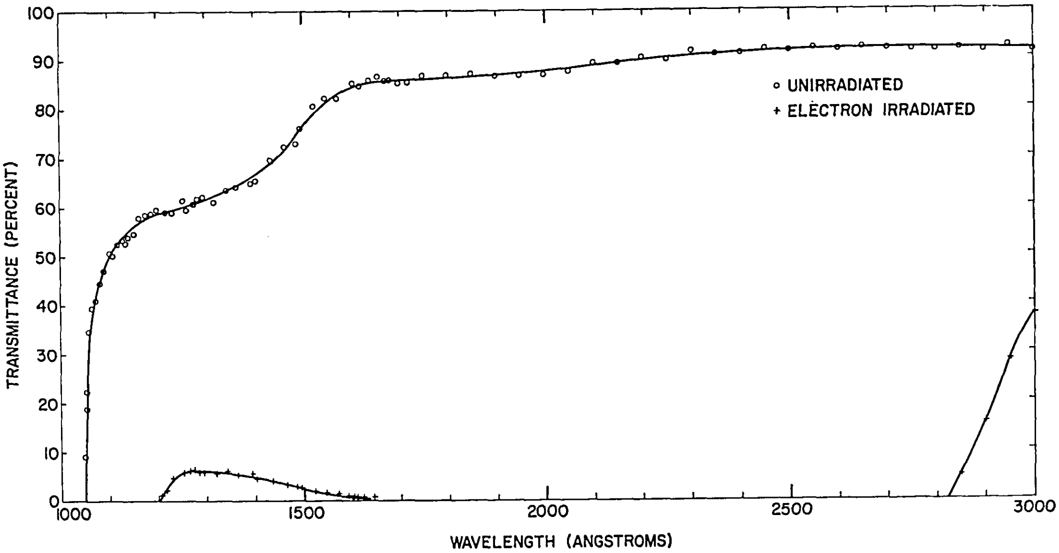

Fig. 1. Transmittance of LiF before and after irradiation by 10^{14} electrons/cm² at 1.0 MeV and at 2.0 MeV.

trons/cm² at 2.0 MeV. Irradiation times were 30 min at each energy.

The synthetic sapphire (α-Al_2O_3) showed the smallest change in transmittance due to electron irradiation. For this reason it was used as an electron shield for the materials listed in Table II. The 6.4-mm thick Al_2O_3 crystal was placed between the incident 2.0-MeV beam and the crystal being irradiated. In a space experiment this would correspond to using a sapphire shield to stop the majority of the high energy electrons in the radiation belt. In this case the principal source of irradiation would be the resulting bremsstrahlung. The total irradiation came from 10^{14} electrons/cm² at 2.0 MeV incident on the sapphire window. No attempt was made to shield the materials listed in Table II from scattered electrons.

All measurements of transmittance were made within a few hours after irradiation. Phosphorescence was detected in all irradiated crystals, although it could not be observed visually. Consequently, corrections were made for this light emission in the measurements of transmittance.

Table I. Optical Material Characteristics

Crystal	[a] (Å)	[b] (mm)	[c]	[d] (Å)	[e]
LiF	1050	2.09		1050–1200, and 1650–2800	Yellow
MgF_2	1130	1.51	90°	1200, 2600	Colorless
CaF_2	1230	3.60		1900, 2250	Violet
BaF_2	1335	1.10		2500	Blue tint
Al_2O_3	1435	6.41	60°	2050[f], 2650, >2950	Beige
SiO_2	1595	6.46		1650, 2150	Colorless

[a] Ultraviolet transmission limit.
[b] Thickness.
[c] Angle of c axis with electron beam for birefringent crystals.
[d] Radiation-induced absorption features.
[e] Color after irradiation.
[f] Transmittance increases with irradiation.

IV. Transmittance Changes from Electron Irradiation

A. Lithium Fluoride

The sample measured was an optically polished, high-purity, synthetic crystal made by the Harshaw Chemical Company. The transmittance before and after irradiation is given in Fig. 1. Obviously LiF is a poor candidate for use in space optics in a high energy radiation environment. Even though the crystal has turned bright yellow, there is a band that remains slightly transparent from 1200 Å to 1650 Å. For the important solar hydrogen Lyman α line at 1216 Å, the transmittance has decreased from 60% to 2%. Beyond 2800 Å it increases rapidly to 33% at 3000 A.*

These absorption features can be bleached out by heating to 400°C for several hours. Unfortunately, at present, the power necessary to do this on an earth satellite would be a practical limitation.

B. Magnesium Fluoride

The sample used was a high-purity crystal grown and optically polished by the Harshaw Chemical Company. It only has been within the past few years that MgF_2 crystals have been available which transmit below 1300 Å. From Fig. 2 it can be seen that the crystal begins transmitting at 1130 Å, and that it has a transmittance of 529Å at hydrogen Lyman α. Under electron irradiation two distinct absorption bands develop. The strongest absorption band is at 2600 Å while a con-

* For detailed information on the radiation-induced absorption features in the far uv, see the work of Uchida *et al.*[2]

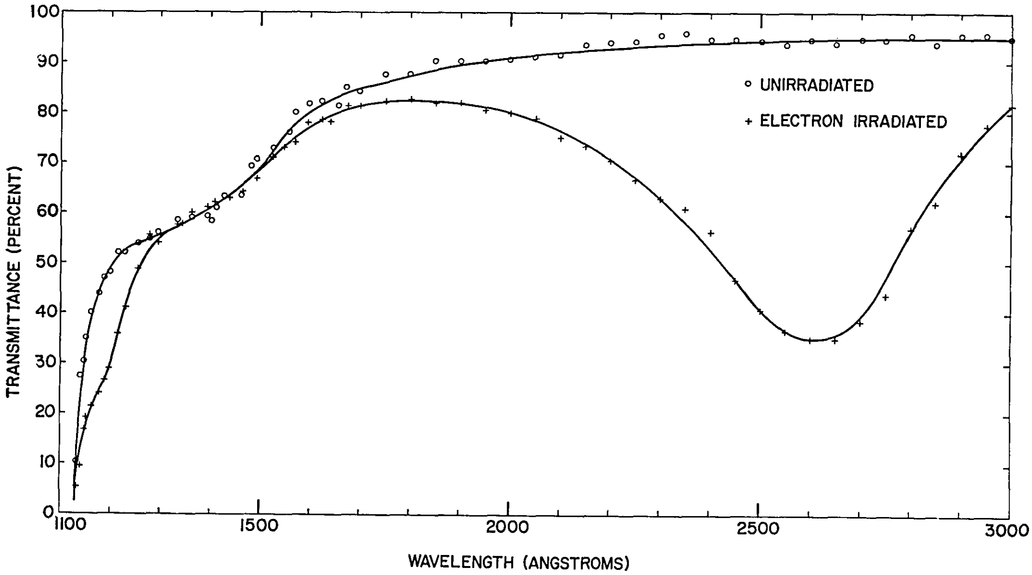

Fig. 2. Transmittance of MgF_2 before and after irradiation by 10^{14} electrons/cm^2 at 1.0 MeV and at 2.0 MeV.

siderably weaker one is definitely present at 1200 Å. The band at 2600 Å is a well-known feature.*

Even with this weak radiation-induced absorption feature at 1200 Å, the transmittance at Lyman alpha has decreased only from 52% to 36%. This is certainly a modest reduction when compared to the reduction in transmittance of a factor of thirty in LiF in the same radiation environment.

Magnesium fluoride has the added advantage of being considerably less soluble in water than LiF (0.013 vs 0.27 g/100 g of H_2O). Note also that no change in transmittance is observed in the 1300–1600 Å region.

C. Calcium Fluoride

This synthetic crystal from Harshaw was polished in the optical shop at GSFC. Under electron irradiation the sample developed a strong violet color. From the transmittance curves of Fig. 3, it can be seen that the effects of irradiation are least pronounced in the vicinity of the short wavelength limit. As one goes to longer wavelengths, the absorption becomes stronger. Two distinct absorption features occur at 1900 Å and 2250 Å. It also appears that another feature is developing as one approaches 3000 Å, which is probably the α band at 3700 Å.[4]

D. Barium Fluoride

This crystal appears to be highly resistant to radiation except for a small amount of absorption above 2500 Å which can be seen in Fig. 4. Barium fluoride may be useful not only as a filter material but also as the low index-of-refraction element of an achromat for the vacuum uv.

* For information on the properties of MgF_2 crystallized from the melt, see the work of Duncanson and Stevenson.[3]

The curves in Fig. 4 are at variance with the work of Messner and Smakula[5] on the absorption of BaF_2 colored by 3-MeV electrons at 20°C. They show a major absorption band at 2000 Å, but only a minor one at 2500 Å. The reason for discrepancy between the two measurements is not known.

E. Sapphire

In Fig. 5, transmittance curves are given for three conditions for Linde polished uv grade synthetic sapphire (α-Al_2O_3). The curves are given for these cases: unirradiated, 10^{14} electrons/cm^2 at 1.0 MeV plus 10^{14} electrons/cm^2 at 2.0 MeV, and for a total dose of 2×10^{14} electrons/cm^2 at 1.0 MeV and 7×10^{14} electrons/cm^2 at 2.0 MeV. The only observed losses in transmittance are possibly a small decrease at 2600 Å and beyond 2950 Å. The weak absorption at 2600 Å and the slight decrease in transmittance above 2950 Å may correspond to induced absorptions by reactor irradiations at 2554 Å and 3000 Å as reported by Levy.[6]

Strangely enough, the well-known strong absorption band at 6.06 eV (2040 Å) is not observed. One ob-

Table II. Optical Material Characteristics

Crystal	^{a} (Å)	^{b} (mm)	^{c}	^{d}	^{e}
SiO_2 (Corning)	1580	3.29		1900 Å^f	Colorless
SiO_2 (Dynasil)	1590	2.04		1900 Å^f	Colorless
ADP	1780	2.99	0°	1900 Å?	Colorless
Calcite	2030	2.25	45°	None	Colorless
Corning 9-54	2185	2.22		All	Grey
Corning 7-54	2270	3.02		All	Black

^{a} Ultraviolet transmission limit.
^{b} Thickness.
^{c} Angle of c axis with electron beam for birefringent crystals.
^{d} Radiation-induced absorption features.
^{e} Color after irradiation.
^{f} Transmittance increases with irradiation.

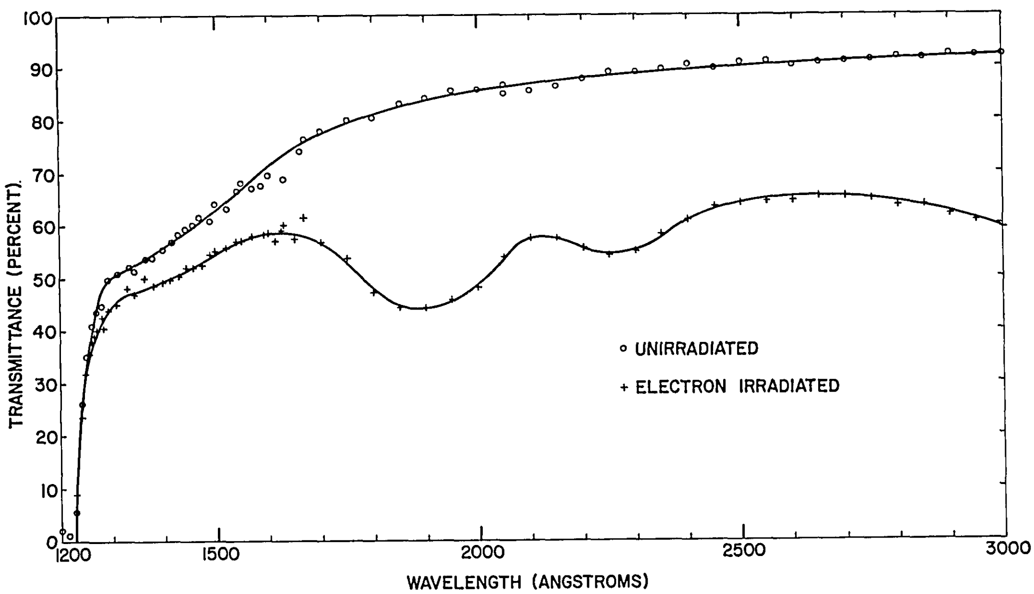

Fig. 3. Transmittance of CaF_2 before and after irradiation by 10^{14} electrons/cm^2 at 1.0 MeV and at 2.0 MeV.

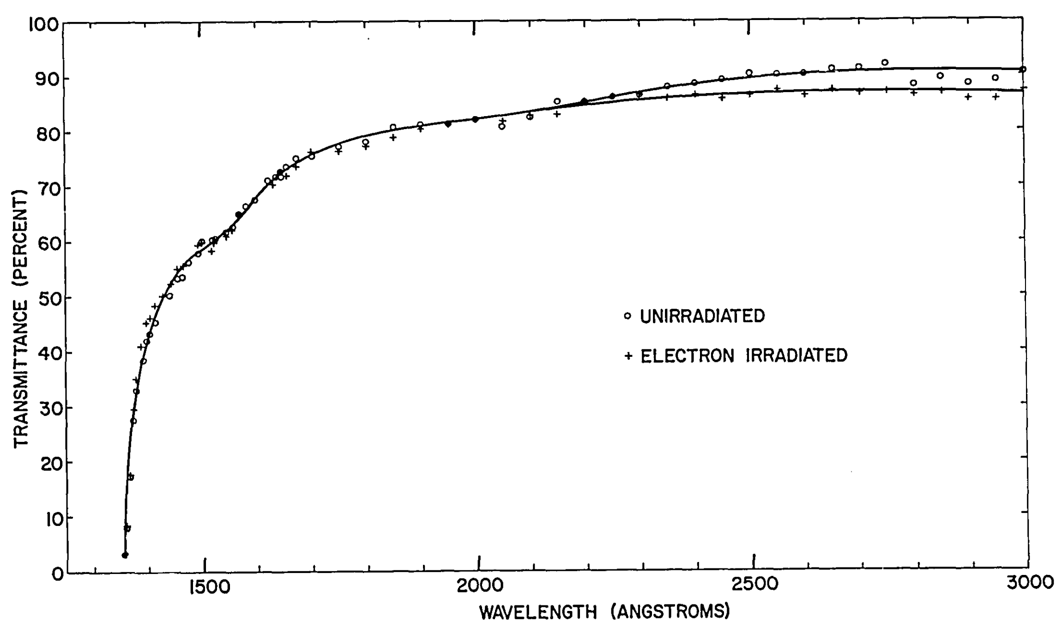

Fig. 4. Transmittance of BaF_2 before and after irradiation by 10^{14} electrons/cm^2 at 1.0 MeV and at 2.0 MeV.

serves at this energy instead of increasing absorption, increasing transmittance with increasing electron irradiation. This phenomenon, an increase in transmittance with irradiation, has been observed by Levy[6] in the lower energy region of 3 to 1 eV.

From these measurements one may conclude that synthetic sapphire is highly resistant to high-energy electron irradiation such as one encounters in the lower regions of the radiation belts. Hence, Al_2O_3 should be useful for shielding those optical materials that are sensitive to radiation damage provided that the short wavelength limit of transmission of sapphire can be tolerated. Synthetic sapphire might also be useful as the high-index element with BaF_2 as the low-index element in an achromat for use in the 1450–3000-Å region.

F. Fused Silica

Whereas the sample of Al_2O_3 remained relatively unaffected by electron irradiation in the uv but became slightly beige in color, the sample of high-purity fused silica (Dynasil optical grade) remained perfectly clear while undergoing a considerable change in transmittance below 3000 Å. This is clearly seen in Fig. 6.

The most prominent radiation-induced feature is the C band at 2150 Å. Even though it is not too obvious, one can see that the radiation-induced absorption coefficient increases as one goes to wavelengths below 1800 Å. The maximum of the absorption that appears to lie between 1670 Å and the cutoff at 1600 Å is the E band. Nelson and Weeks[7] have shown that synthetic crystal quartz is more resistant to the production

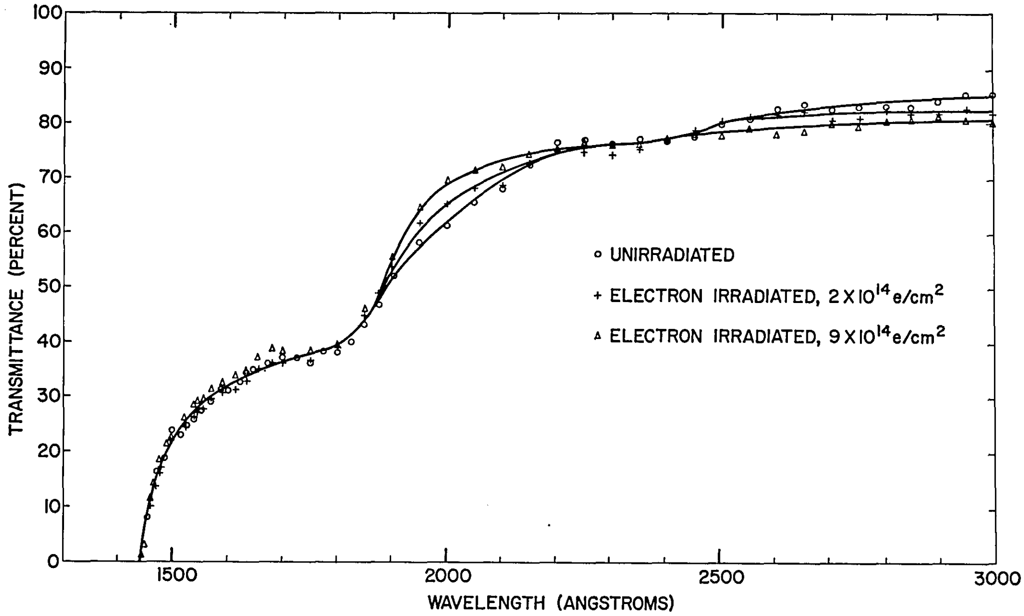

Fig. 5. Transmittance of Al_2O_3 before, and after irradiation by 10^{14} electrons/cm^2 at 1.0 MeV and at 2.0 MeV, and after irradiation by 2×10^{14} electrons/cm^2 at 1.0 MeV and 7×10^{14} electrons/cm^2 at 2.0 MeV.

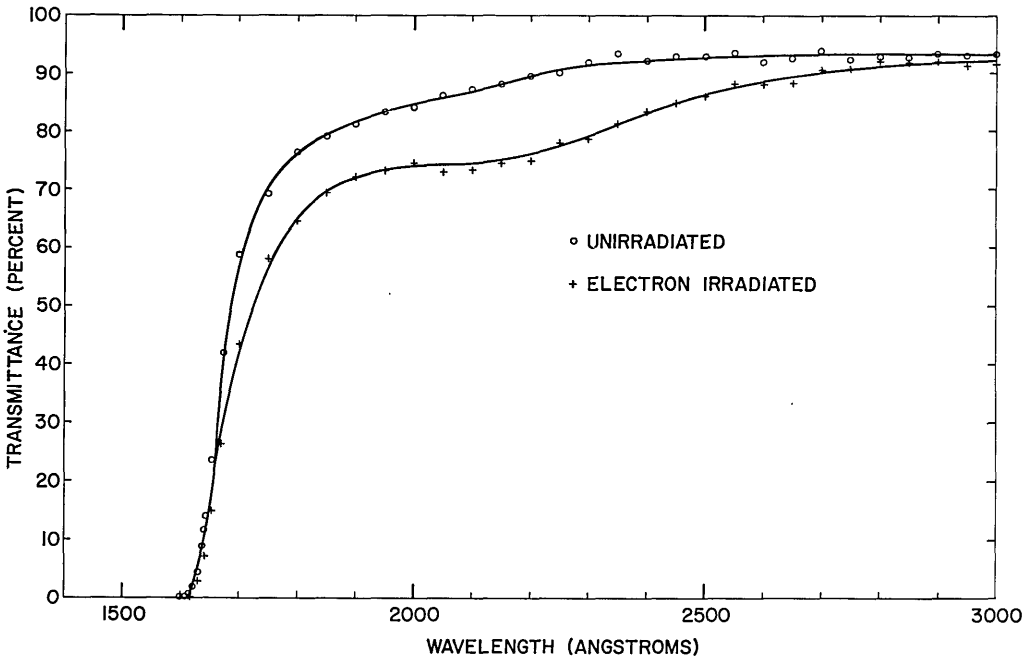

Fig. 6. Transmittance of fused SiO_2 before and after irradiation by 10^{14} electrons/cm^2 at 1.0 MeV and at 2.0 MeV.

of the C band, whereas the E band is produced equally readily in either crystal quartz or fused silica.

From these measurements it is apparent that great caution should be used if one intends to use fused silica in a high energy electron environment to transmit wavelengths below 2800 Å.

V. Transmittance Changes in Electron Shielded Materials

From the measurements made on the crystals listed in Table I, it is concluded that synthetic sapphire is the best choice for shielding the more radiation sensitive elements from high energy electrons. For the materials listed in Table II, the 6.4-mm thick synthetic sapphire was placed between the 2-MeV electron beam and the particular sample being irradiated. The range of 2.0-MeV electrons in sapphire is about 3.7 mm. The total dose for each sample was 10^{14} electrons/cm^2 at 2.0 MeV incident on the sapphire.

A. Fused Silica

Two high purity samples were measured. These were Corning 7940 and Dynasil 1850Å. The transmittance curves in Figs. 7 and 8 show some evidence of having increased after irradiation in the region 1800–1950 Å. This effect is close to the accuracy of the

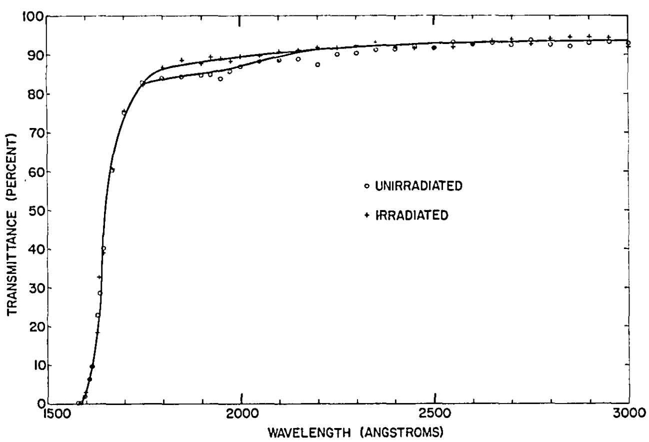

Fig. 7. Transmittance of Corning 7940 fused SiO_2 before and after irradiation resulting from 10^{14} electrons/cm^2 at 2.0 MeV incident on a sapphire shield.

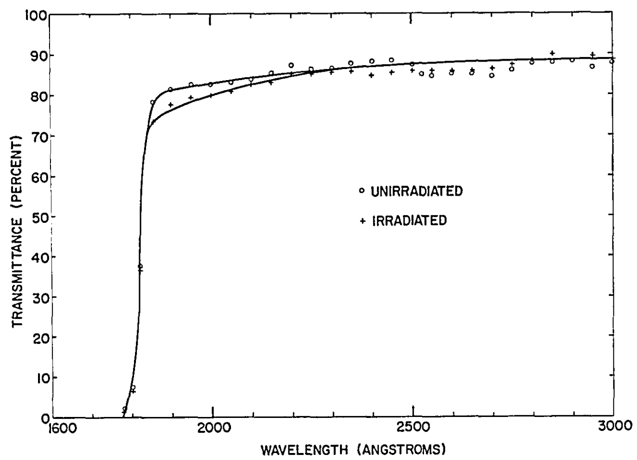

Fig. 9. Transmittance of ADP before and after irradiation resulting from irradiation resulting from 10^{14} electrons/cm^2 at 2.0 MeV incident on a sapphire shield.

measurements and may not be real, although it is rather surprising that it appears in both samples. From these measurements it appears that fused silica can be used as a uv optical element in space if it is properly shielded from high energy electrons.

B. ADP

This ammonium dihydrogen phosphate crystal was grown and polished by the Harshaw Chemical Company. The crystal has an extremely sharp uv cutoff at 1800 Å, and it shows practically no change in transmittance after being irradiated as can be seen in Fig. 9. There is the possibility that there is a small amount of radiation induced absorption between 1850 Å and 2050 Å. However, the conclusion is that ADP is useful for space optical uses below 3000 Å.

One does encounter certain problems in attempting to use this crystal as it is fairly hygroscopic, and it is also sensitive to thermal shock. For example, in one crystal that was quite warm after electron irradiation, an extensive crack developed across the face when it was touched at the edges.

C. Calcite

The crystal of high optical quality was optically polished by the Harshaw Chemical Company. No radiation-induced absorption is observed in the transmittance curves in Fig. 10. Therefore, one concludes that calcite when properly shielded from electrons is suitable for space use.

D. Corning 9–54

This is the familar Vycor (7910), a high-silica-content glass that was observed visually to have turned grey

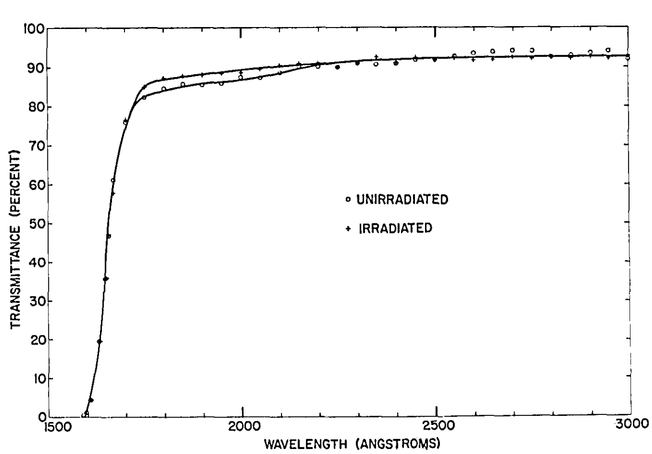

Fig. 8. Transmittance of Dynasil 1850A fused SiO_2 before and after irradiation resulting from 10^{14} electrons/cm^2 at 2.0 MeV incident on a sapphire shield.

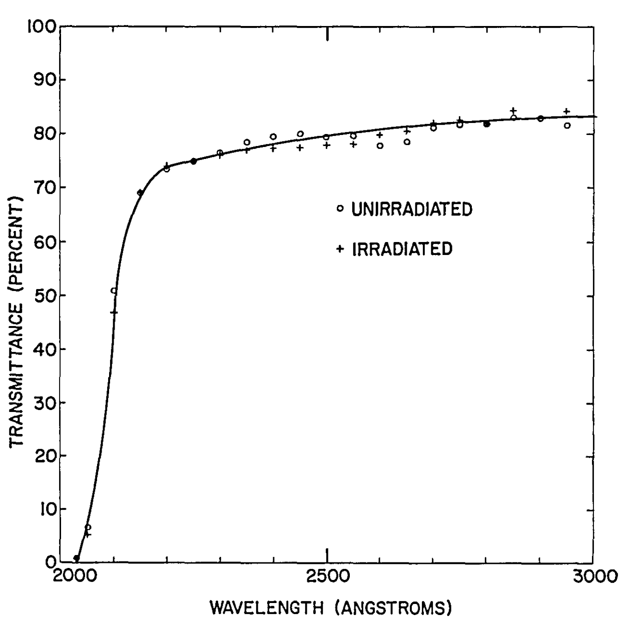

Fig. 10. Transmittance of calcite before and after irradiation resulting from 10^{14} electrons/cm^2 at 2.0 MeV incident on a sapphire shield.

after irradiation. From Fig. 11 it can be seen that the transmittance is strongly affected below 3000 Å. Hence, one should be cautious about using it in space for extended periods.

E. Corning 7–54

This familiar, black, uv-transmitting glass darkened rapidly in the radiation environment as can be seen in Fig. 12. Since this Corning glass (9863) is also known to darken upon exposure to intense uv radiation, it is apparent that this is a poor material for optical use in space.

VI. Conclusions

It was the purpose of this work to investigate the effect on transmittance of a high-energy electron environment on a number of optical materials which transmit in the 1050–3000-Å region. Having subjected these materials to the same radiation dose, it is possible to make recommendations as to which are best suited for use in space applications.

Of the materials listed in Table I, MgF_2, BaF_2, and Al_2O_3 appear to have the greatest potential for space applications. Magnesium fluoride should prove to be especially valuable because of its high transmittance at the hydrogen Lyman α line as well as its birefringence. In fact, polarizers have been made for the vacuum uv utilizing MgF_2.[8]

Barium fluoride and synthetic sapphire might be useful as elements in an achromat. However, care must be exercised in its use. Recent work by Malitson *et al.*[9,10] shows that not only are there radiation effects on transmittance but also on the index of refraction. Unfortunately the indices of refraction of most uv transmitting materials are poorly known.

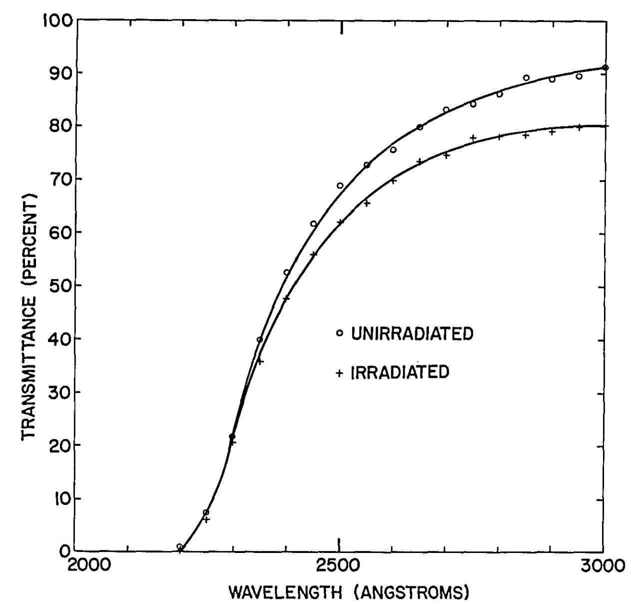

Fig. 11. Transmittance of Corning 9–54 (Vycor) before and after irradiation resulting from 10^{14} electrons/cm^2 at 2.0 MeV incident on a sapphire shield.

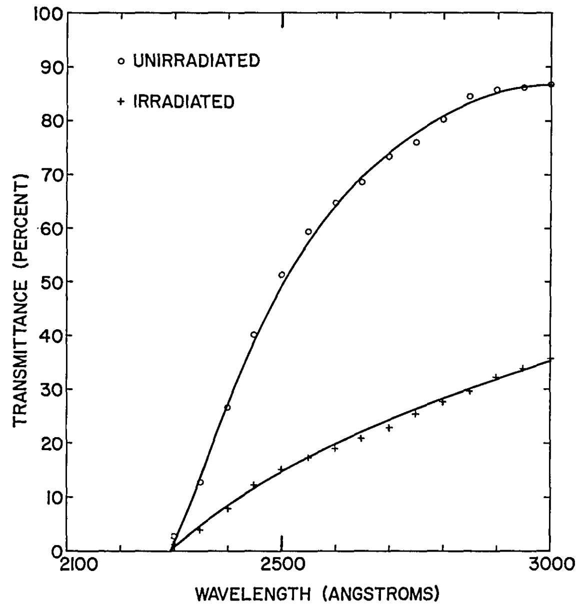

Fig. 12. Transmittance of Corning 7–54 before and after irradiation resulting from 10^{14} electrons/cm^2 at 2.0 MeV incident on a sapphire shield.

All the materials except Corning Glasses 9–54 and 7–54 appear to be suited for space use if the proper precautions are taken to shield them from direct electron irradiation in space. The crystals, ADP and calcite, which are birefringent also would be useful as uv polarizers.

We would like to thank the Harshaw Chemical Company for samples of MgF_2, the Corning Glass Company for samples of 9–54 and 7940 fused silica, the Astrophysics Branch at GSFC for samples of BaF_2, and 7–54, the Dynasil Corporation for fused SiO_2, and Steve Olfky of the W. R. Grace Company for his assistance in the electron irradiations.

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