# Radiation-induced transmission degradation of borosilicate crown optical glass from four different manufacturers

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**Abstract.** Space-borne optical systems must be tolerant to radiation to guarantee that the required system performance is maintained during prolonged mission times. We show that the radiation hardness can be improved by selecting the relevant glass from a group of optical analogs. This conclusion is based on the study of gamma-radiation-induced absorption of crown glasses from group 517640 (glasses with $n_d \approx 1.517$ and $\nu_d \approx 64$)—BK7 and NBK7 (Schott), S-BSL7 (Ohara), BSC 517642 (Pilkington), and K8 (NITIOM). Our results show that whereas these glasses are optical analogs before irradiation, they behave differently during and after irradiation.  [DOI: 10.1117/1.2722322]

Subject terms: radiation effects; crown optical glass; space optics.

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## 1 Introduction

An important requirement for space-borne optical systems is the capability to withstand the adverse impact of space radiation.[1,2] This requirement limits the list of candidate materials and may result in a significant problem when a complicated optical system, sometimes based on tens of different glasses, must be designed.[3]

From the point of view of an optical engineer, optical glass is characterized by its refractive index and dispersion at the working wavelength(s). Very often glass with the required characteristics is available from different manufacturers. Such glasses are termed "optical analogs," and tables are available that enable finding a substitution. When using optical glasses in a benign environment, e.g., out of any radiation field, small differences in the optical properties are of secondary importance. An optical system can usually be adjusted to account for those differences without complete redesign. However, optical analog glasses are fabricated based on proprietary technology and are different in terms of the chemical composition as well as in the level of technological impurities. From the point of view of the radiation hardness, those differences can play a role because even a very small concentration of certain ions significantly influence the sensitivity of glass to radiation.[4–6]

To the best of our knowledge the problem or relative radiation sensitivity of optical analogs was addressed only for the case of pairs "normal–radiation-hardened analog," when the radiation hardening is achieved via doping with cerium.[7] The use of radiation-hardened analogs is not always desirable because cerium-doped glasses have a reduced transmission in the blue. In addition, radiation-hardened glasses are being discontinued from optical catalogs, and their procurement becomes increasingly difficult and expensive. The possibility to improve the radiation hardness of the optical system by selecting between standard analogous glasses from different manufacturers then became interesting.[8]

In this paper we therefore compare the radiation sensitivity of frequently used crown silicate glasses with $n_d \approx 1.517$ ($\lambda_d$=587.56 nm) and $\nu_d \approx 64$, i.e., glasses that all correspond to the 517640 group (international classification) but come from different manufacturers. The following glasses were tested: BK7 from Schott and its replacement NBK7 ($n_\mathrm{d} \approx 1.51680$, $\nu_\mathrm{d} \approx 64.17$), S-BSL7 from Ohara, BSC 517642 from Pilkington, and K8 ($\mathrm{n}_d \approx 1.51637$, $\nu_d \approx 64.07$) from NITIOM (Institute of Optical Materials Science and Technology, St. Petersburg, Russia).

## 2 Experiment

The glass samples were irradiated using $Co^{60}$ sources at dose-rates of 0.6, 2.8, and 190 krad/h, respectively. The SI

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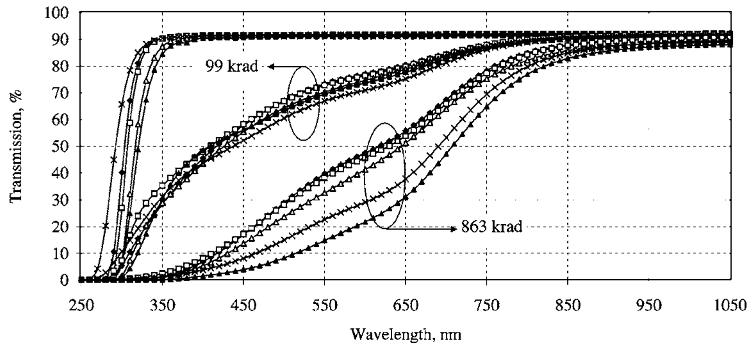


**Fig. 1** Transmission spectra of 5-mm-thick samples; curve marking corresponds to ♦, NBK7; □, BK7; △, BSC; ×, S-BSL7; and ▲, K8. The upper set of curves is the initial transmission, the middle and the lower are after exposure to 99 and 863 krad at 2.4 krad/h, respectively.

unit of absorbed dose is the gray, which corresponds to 1 J of energy absorbed by 1 kg of material while the rad is traditionally used by the space community; 1 Gy = 100 rads. For the low-dose-rate irradiation, the dose was monitored with a Nuclear Enterprises Ionex Dosemeter 2000 with a 0.6-$cm^3$ ion chamber with the dose referred to water. For the high-dose-rate environment, Red Perspex 4034 dyed PMMA was used. The irradiations were performed at room temperature following a dose-step accumulation approach already described in details.[9] First, glass samples were irradiated up to a fraction of the total dose. The transmission spectra were measured with a delay of at least 2 h after the end of the irradiation step. The irradiation-measurement cycle was repeated several times until a total dose (173, 863, and 600 krad for the dose rates already listed, respectively) was accumulated. The selection of the total dose level stems from the possible use of the results for the prediction of radiation-induced performance degradation of space-borne optical instruments. For near-Earth space a 1-Mrad dose is often considered as a figure of merit. Such a dose corresponds to a 1-y exposure on a geostationary transfer orbit (GTO) behind a 2-mm Al spherical shield.[1]

After irradiation the samples were stored in uncontrolled laboratory conditions with possible temperature variations in a range from 15 to 25 °C. To assess the effect of postradiation annealing, transmission spectra were measured a number of times after the end of irradiation with progressively increasing (approximately by a factor of 2) intervals between the measurements. The last measurement was carried out 900 days after the start of the experiment.

Transmission measurements were performed with a commercial double-beam UV-visible-near-IR (UV-Vis-NIR) spectrophotometer over a spectral range from 200 to 1500 nm. The absolute accuracy of the transmission measurements was better than 0.5%. The size of the probing beam in the spectrophotometer ($4 \times 12\ mm^2$) is smaller than the size of the samples. Fiducial marks on the samples enabled us to preserve the same sample orientation and to probe the same part during all transmission measurements.

Care was taken to avoid contaminations of the sample surfaces. Special holders enabled installing the samples in the irradiators without direct contact with the samples. During irradiation the samples were not protected. After irradiation they were wrapped in optical paper and stored in carton boxes. Before each measurement, the samples were visually inspected and if necessary cleaned using ethanol and demineralized water.

Our primary interest is to study radiation-induced transmission changes in the visible range. However, data in the UV are required to understand the underlying physical mechanisms. The initial absorption of multicomponent glasses grows very quickly in the UV. This necessitates measuring relatively low transmittance changes in a spectral region where the initial optical density of the sample is already very high. The use of thin samples enables circumventing this problem. Very thin samples are not suitable for induced attenuation measurements in the visible, where for the Megarad-dose-level radiation-induced absorption in the studied glasses was expected to be relatively low. In that region, samples of centimeter-range thickness were required. Therefore, two types of samples were prepared. Those were disks of approximately 0.15- and 4.5-mm thickness and ~30 mm in diameter, with the K8 sample being slightly thicker (5.3 mm) with optical quality polished sides. A safe handling of very fragile 0.15-mm samples was made possible owing to their mounting on metallic rings using radiation-resistant glue. Cleaning of these samples remained a delicate operation, which was performed only if surface contamination on the test area was visible.

## 3 Results and Discussion

Figure 1 shows transmission spectra of the thick glass samples from the UV to the NIR range. For wavelengths longer than 400 nm, the initial transmission curves were accounted by the Fresnel reflection and differ by less than 0.5%, in agreement with their definition as glasses from the 517640 group. However, the difference in the 50% transmission wavelength is more than 30 nm for the two limiting cases of S-BSL7 and K8, indicating that the chemical composition of these glasses is indeed not the same. Noted also that the amplitudes of the dips at 1410 nm related to the overtone of the OH group oscillations (not shown in the figure) are also slightly different. Therefore, the radiation sensitivity should also be different, as evidenced by data for 99 and 863 krad. At 99 krad the difference between the

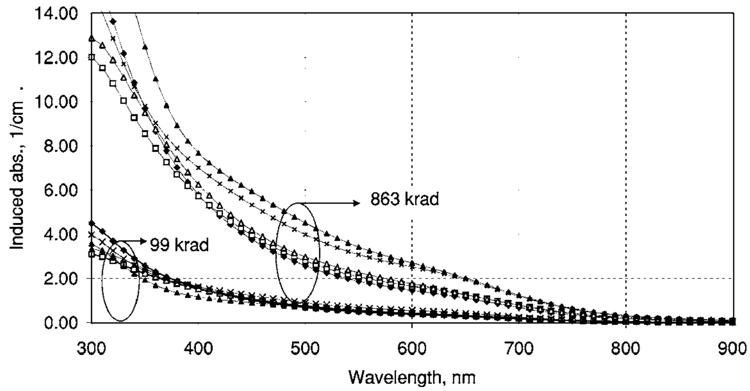


**Fig. 2** Induced absorption spectra of 5-mm-thick samples for 2.4-krad/h dose-rate irradiation: ♦, NBK7; □, BK7; △, BSC; ×, S-BSL7; and ▲, K8.

most and the least sensitive glasses is less than 10%. With increasing dose up to 863 krad the difference is getting more significant.

It was already mentioned that the studied samples have slightly different thicknesses. The refractive index is not exactly the same either. The influence of those differences on the assessment of the sensitivity to radiation can be eliminated by performing the analysis in terms of the induced absorption spectrum (IAS), which is defined as the (natural) logarithm of the ratio of the transmission before irradiation ($T_0$) to that after irradiation ($T_i$) normalized by the sample thickness $L$:

$$\Delta\alpha(\lambda) = (1/L) \ln [T_0(\lambda)/T_i(\lambda)]. \tag{1}$$

Figure 2 shows that, in fact, K8 has the lowest induced absorption coefficient at 99 krad, while at 863 krad, the situation is inverted. The IAS for NBK7, BK7, and BSC are not very different at both doses, while K8 and S-BSL7 follow apart at 863 krad. NBK7 is a replacement of BK7, and before irradiation the optical properties of those two glasses are almost identical. However, the radiation sensitivity is different, as is easily detectable in the UV.

The behavior of the K8 can be explained using the analogy with the protecting action of $CeO_2$, which is usually added to make glasses more radiation resistant when the transmission in the visible is of concern.[7] It appears that the level of technological impurities and defect precursors in K8 is the highest among the studied glasses. This is confirmed by the observation that for K8 the 50% transmission in the UV is shifted to longer wavelengths as compared to other glasses (Fig. 1). Its transmission spectrum in the 400 to 900-nm range also has a weak structure (not distinguishable in Fig. 1), which is an indication of some contaminations. Usually such technological impurities easily trap charge carriers, preventing the formation of other color centers. If the associated absorption bands are located in the UV, the transmission in the visible is preserved, as happen in the case of $CeO_2$ addition. This may explain why for 99 krad, the induced absorption for K8 is slightly lower than for other glasses. However, the concentration of impurities can not be high, their protection capacity is quickly exhausted with the dose increase, and the induced absorption builds up.

Figures 3 and 4 show IAS for two other dose rates. The difference between the maximal and the minimal dose rates is more than two orders of magnitude, but the shape and the amplitude of the spectra are consistent with the total ionizing dose effect.

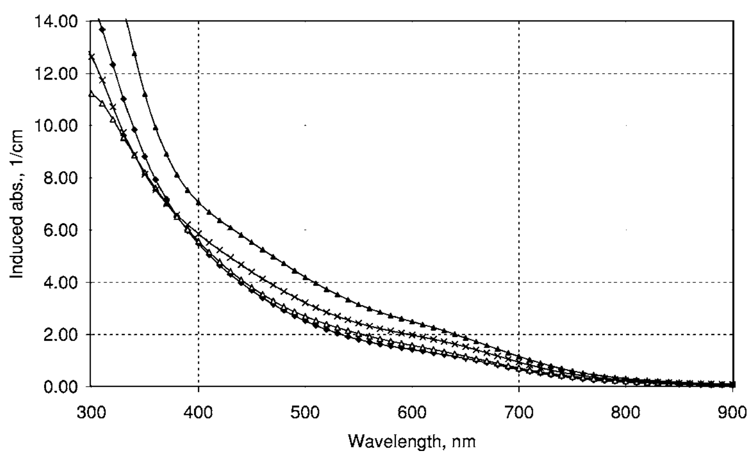


**Fig. 3** Induced absorption spectra of 5-mm-thick samples after high-dose-rate (200 krad/h) irradiation up to 600 krad; curve marking corresponds to ♦, NBK7; △, BSC; ×, S-BSL7; and ▲, K8.

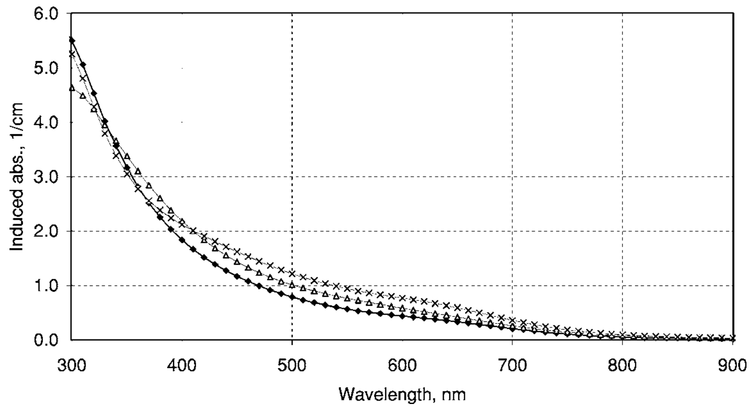


**Fig. 4** Induced absorption spectra of 5-mm-thick samples after 0.6 krad/h dose rate irradiation up to 173 krad: ♦, NBK7; △, BSC; and ×, S-BSL7.

Figures 2–4 show that the radiation sensitivity grows in the UV. However, the strong initial absorption prevents to obtain data for wavelengths shorter than 300 nm. As explained in the previous section, thinner samples were used to circumvent this problem. Figure 5 shows an example of an IAS obtained on 0.15-mm-thick samples. All samples show a negative induced absorption band(s) in the deep UV, an effect already discussed[9] for BK7. For BK7 and NBK7 the IAS practically coincide for wavelengths longer than 400 nm, and they differ significantly for shorter wavelengths. Therefore, NBK7 and BK7 remain analogs after irradiation when the transmission in the visible is of concern, but not in the UV. Strictly speaking, the radiation-induced refractive index changes[10] in the visible will also be different due to differences in the UV absorption. It may be expected that the index changes are stronger for NBK7. On the absolute scale those changes should be less than $10^{-4}$ for all studied glasses and can be neglected.

Separating the contributions of different radiation defects usually helps to understand the origin of the radiation sensitivity. A standard way to tackle this problem is to decompose IAS into individual Gaussian absorption bands.[9] However, the Gaussians are nonorthogonal, and such a decomposition is an ill-defined problem, which requires additional information to carry it out in a justified way. Recently, we have proposed a kinetic approach to this problem.[11] The idea of the approach is to perform the decomposition using correlations between IAS obtained on the same sample in the course of a multistep irradiation and long-term postirradiation annealing.

The dose levels below 1 Mrad considered in our work correspond to defect concentrations lower than $10^{19}$ cm$^{-3}$. At such relatively low concentrations, we can neglect interactions between radiation-induced defects. Therefore, the spectroscopic parameters (peak position and the bandwidth) of the induced absorption bands should remain practically unchanged during irradiation and postirradiation annealing. This enables us to perform a "correlated" analysis of a series of induced optical absorption spectra obtained on a single or on several similar samples for consecutive radiation dose steps and during long-term postirradiation annealing. For each IAS the spectroscopic band, parameters are defined by other spectra and only the band amplitudes are allowed to vary. In addition, the amplitude of radiation-induced absorption bands should show a physically reasonable variation, e.g., grow with the dose accumulation, shrink after the end of irradiation, and not show irregular changes.

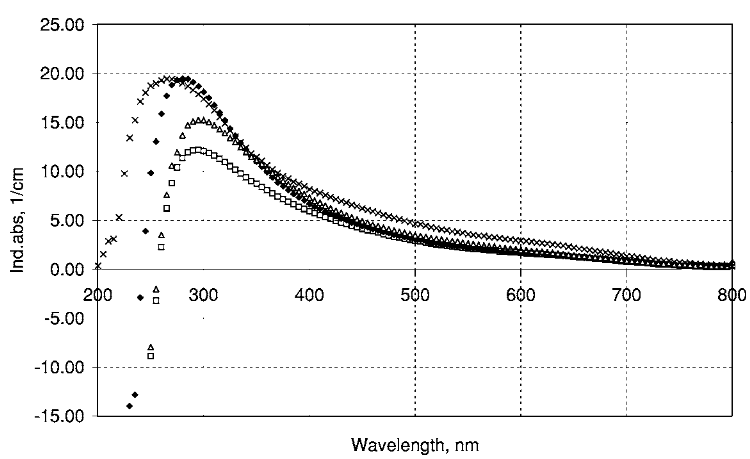


**Fig. 5** Induced absorption spectra of thin samples after low-dose-rate irradiation up to 863 krad as measured 574 days after the end of irradiation: ♦, NBK7; □, BK7; △, BSC; and ×, S-BSL7.

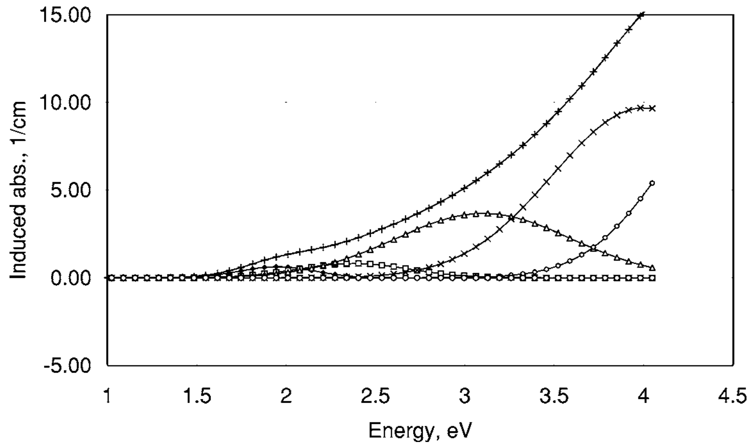


**Fig. 6** Example of the decomposition of an IAS (NBK7, $D=863$ krad) into individual absorption bands. The maximal difference between the experimental (solid line) data and the synthesized curve (line marked with +) is 0.05 $cm^{-1}$ and the average difference is 0.006 $cm^{-1}$. The curves marked with solid diamonds, open squares, open triangles, crosses, and open circles show the contributions of the bands 1 to 5, of which the parameters are given in Table 1.

We applied the kinetic approach to analyze the data obtained for the studied samples. For each glass ~40 IAS where decomposed in the correlated manner. It was found that the use of six Gaussian bands:

$$G(E) = A \exp[-(E-E_0)^2/2\sigma^2]/(\sigma\sqrt{2\pi}), \tag{2}$$

where $A$ is the band amplitude, $E_0$ is the band maximum, and $\sigma$ is the dispersion (band width), enables a good approximation of the IAS. Figure 6 shows an example of such a decomposition. The average mean square root deviation between measured and simulated data was below 0.02 $cm^{-1}$ for all spectra (0.006 $cm^{-1}$ for N-BK7 and BK7). The parameters for the absorption bands of the studied glasses are given in Table 1. For K8, the parameters of only five bands are given in Table 1 because measurements on only 5-mm-thick samples did not enable us to obtain data for the deep UV spectral range, and therefore five bands were taken to describe the experimental data.

Based on computations performed with different initial guess values and convergence parameters[11] the accuracy of the band parameters can be estimated as being better than ±0.05 eV. No *a priori* information was used to carry out the decomposition. Nevertheless, the obtained values are in agreement with already published data,[4,6] where the band parameters were found based on modifying the chemical composition of the glasses and the irradiation conditions.

It was already discussed that with the kinetic approach based on the data for isothermal annealing strongly overlapping or very weak absorption bands may remain unresolved.[11] However, for the purpose of comparing the results for analogous glasses, the most important issue is the differences in the band parameters and not the absolute values. We therefore assume that Table 1 can be used to interpret the differences in radiation sensitivity of our glasses.

First we compare NBK7 and BK7. The same initial

**Table 1** Parameters for Gaussian-induced absorption bands found via the correlated decomposition of the IAS for 2.4-krad/h dose-rate irradiation.

| | Band Maximum $E_0$ (eV) | | | | | Band half-width $\sigma$ (eV) | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Band | NBK7 | BK7 | BSL7 | BSC | K8 | NBK7 | BK7 | BSL7 | BSC | K8 |
| 1 | 1.95 | 1.94 | 1.95 | 1.96 | 1.95 | 0.21 | 0.20 | 0.18 | 0.21 | 0.18 |
| 2 | 2.37 | 2.31 | 2.30 | 2.35 & 2.43 | 2.32 | 0.31 | 0.32 | 0.28 | 0.28 & 0.94 | 0.30 |
| 3 | 3.11 | 3.14 | 3.24 | 3.11 | 3.12 | 0.49 | 0.52 | 0.66 | 0.52 | 0.62 |
| 4 | 4.01 | 3.99 | 4.12 | 3.85 | 3.86 | 0.51 | 0.48 | 0.44 | 0.45 | 0.37 |
| 5 | 4.57 | 4.57 | 4.96 | 4.36 | 4.39 | 0.46 | 0.40 | 0.58 | 0.56 | 0.51 |
| 6 | 5.47 | 5.12 | 5.80 | 5.19 | | 0.24 | 0.23 | 0.30 | 0.31 | |

guess values and the computation parameters were used. Table 1 shows that the parameters for bands 1 to 5 are practically identical. Therefore, the dissimilarity in the radiation sensitivity in the visible range is related to differences in the defect generation efficiency, which in turn must be related to the presence of some other defects, such as the $E'$ center and Fe ions, which have absorption bands outside the visible range. Indeed, the maximum of the band responsible for the negative induced absorption in the UV is located at 5.47 eV for NBK7 and at 5.12 eV for BK7. It is very likely that more than one band is responsible for the absorption in the wavelength range below 250 nm (5 eV). There are several radiation-induced centers which can potentially contribute to both positive and negative induced absorption in this range.[5,6] Our data do not enable us to resolve such bands, and the parameters for the sixth band are very probably not accurate. On the other hand, the spectra were taken on identical samples irradiated simultaneously and the difference in the position of the band indicates that the UV centers are responsible for the differences in the radiation response in the visible range. In particular, the UV sensitivity depends on the OH group concentration. The absorption dip at 1.41 $\mu$m related to the OH group overtone is indeed about two times stronger for NBK7 than for BK7.

The parameters of the two low-energy bands 1 and 2 are similar for all five glasses. With the peak wavelength decrease, the band parameters begin to differ. For BSC glass, it was also necessary to add an additional weak broad band centered at 2.43 eV to obtain an accuracy of the absorption spectra fit similar to that obtained for BK7 and N-BK7. The large width of that band indicates that it is probably composed of several bands, while the accuracy of our data is not sufficient to resolve this structure.

The conclusion that we can draw from Table 1 is that the differences in the radiation sensitivity are due to the generation of defects specific for each glass glasses. In particular, the level of technological impurities can play an important role.

## 4 Conclusions

We studied the gamma-radiation-induced absorption of crown glasses with $n_d \approx 1.516$ and $\nu_d \approx 64$ produced by different manufacturers. It is known that glasses with different chemical composition can be designed to have practically identical optical properties over a limited wavelength range of interest. Our results show that whereas the studied glasses are optically similar before irradiation, their radiation sensitivity is different. Even BK7 and NBK7 produced by the same manufacturer show differences in the response to radiation. These two glasses remain close analogs after irradiation only when the transmission for wavelengths longer than 400 nm is considered. For shorter wavelengths, a difference in the induced absorption level is observed, which is explained by differences in the defect generation mechanisms.

The conclusion as to which glass of the studied 517640 group is most or least sensitive to radiation depends on the total dose and the spectral range of interest. K8 shows the lowest level of induced absorption at 100 krad and the highest level at 860 krad. It also appears that the dose rate plays a secondary role. In our case, a change by more than two orders of magnitude (from 0.6 to 200 krad/h) did not result in a significant change of the IAS. It can be concluded that the radiation tolerance of an optical system intended for use in the space can be improved by choosing a suitable glass from the same group.

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