ISSN 2433-2216(Online)
JAXA-RR-23-006E

JAXA Research and Development Report

Gamma-ray irradiation of optical glass for the development of LIBS for future planetary missions

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February 2024

Japan Aerospace Exploration Agency

Contents

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Abstract

In-situ chemical analysis has provided fundamental information on the origin and history of planetary bodies. On rocky bodies, laser-induced breakdown spectroscopy (LIBS) has proven its utility over the last decade. LIBS enables quantitative chemical measurement of samples by analyzing emission spectra from laser-induced plasma. We are currently developing a compact LIBS instrument for future landing missions; however, optical glass experiences degradation in transmittance owing to radiation (the browning effect). We conducted gamma-ray radiation experiments using a ^{60}Co source to assess radiation-induced transmittance changes in four optical glass materials (Ohara S-LAM3, S-NBH53V, S-TIM27, and S-TIH53W), including those incorporated in the spectrometer we are developing. We applied irradiation doses of 10–10,000 Gy (1–1,000 krad), which are comparable to 0.5–500 years in Martian orbit. Post-irradiation transmission was measured to evaluate the timescale of the recovery in transmittance. Our results indicate that transmittance across wavelengths of 380−1,000 nm decreases in all tested glass materials, with more pronounced decreases at higher doses and shorter wavelengths. Transmittance levels recovered over time, reaching > 95% of their initial values on 365 days after exposure to a 100 Gy dose. The estimated recovery timescales for the materials were 60–130 days. When subjected to a 100 Gy dose, the overall transmission of our spectrometer remained at > 80% of its original, unirradiated value. This suggests that the glass materials used in our LIBS spectrometer are sufficiently resistant to radiation for planetary exploration missions. This study provides crucial data on the radiation resistance of these glasses, aiding the design of optical instruments intended for use in space exploration missions.

Keywords: Instrument development, LIBS, gamma-ray irradiation, optical glass

1. Introduction

Planetary science is transitioning to a phase characterized by sample return missions, and the Moon is a prominent future target. Large impact basins on the Moon offer valuable insights into the early impact history of the solar system. Isotopic dating of samples from such basins could potentially help to reconstruct the history of the solar system [1,2]. Lunar breccia samples from the Apollo and Luna missions have already provided some information [3,4]; however, the samples do not provide the geological context necessary for understanding the origin of the basins owing to the lack of in situ characterization. In addition, a type of lunar rock known as purest anorthosite (PAN)

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may provide key constraints on the evolution of the lunar crust [5].

For future missions aimed at returning samples from outcrops with well-defined geological context, in situ analysis prior to sampling is crucial. This study focuses on using laser-induced breakdown spectroscopy (LIBS) for this purpose. LIBS is a technique for rapid quantitative chemical analysis based on atomic and ionic emissions induced by laser irradiation. Its efficacy has already been demonstrated during Martian exploration missions [6,7]. LIBS could potentially identify PAN by analyzing its bulk elemental composition.

In developing a LIBS instrument for planetary applications, we identified the need for optical glasses with a high transmittance and high refractive index across near ultraviolet to near-infrared wavelengths (380–800 nm). The lower limit of the wavelength (380 nm) is restricted by the fact that typical manufactured glasses exhibit a decrease in transmittance at around this wavelength. Nevertheless, many elements critical to addressing the variety of lunar rocks, including Fe (382 nm), Ca (393 and 397 nm), Al (396 nm), Mg (518 nm), Na (589 nm), H (656 nm), and K (766, 769 nm), yield intense peaks in this range [8]. In particular, the primary components of anorthite ($CaAl_2Si_2O_8$) produce peaks in the 380–400 nm range.

These wavelengths are also susceptible to a decrease in transmittance due to radiation exposure, which is commonly known as the browning effect [9]. The decrease in transmittance in glass occurs because of an increased number of lattice defects caused by radiation. Radiation-induced defects in silicate glasses exhibit absorption bands centered at 2–6 eV (210–620 nm), with larger decreases in transmittance typically occurring at shorter wavelengths [10], and the transmittance gradually recovers over time as lattice defects recombine [9,11]. Therefore, understanding the effects of radiation on optical glasses is essential to the development of spectroscopic instruments.

We investigated the impact of the expected radiation conditions on four types of optical glass used in the planetary LIBS instrument we developed to evaluate their suitability for in situ lunar sample analysis. We present transmittance data for these previously unexamined glass materials, facilitating the development of optical instruments for space exploration.

2. Methods

2.1. Gamma-ray irradiation experiments

The optical system of our LIBS spectrometer incorporates six types of glass materials: S-TIM27, S-TIH53W, S-NBH53V, S-FSL5, S-BSL7, and S-BSM16, all of which are produced by Ohara (Fig. 1). These glasses were chosen for their high transmittance at 380–800 nm, high refractive index (n_d), and diverse dn/dT values that are essential for achieving an athermal optical system at the temperatures expected on planetary surfaces. We also included S-LAM3, a candidate during the optical design phase. The effects of radiation on four of these seven types had not been studied previously, whereas three had been examined either by Nishino et al. (1998) or Topcon (unpublished proprietary data; Table 1).

We selected four glasses for the irradiation experiments: S-TIM27, S-LAM3, S-TIH53W, and S-NBH53V. All samples were 25.4 mm in diameter and 5 mm thick, and both sides were polished to measure transmittance. Although planetary instruments in orbit

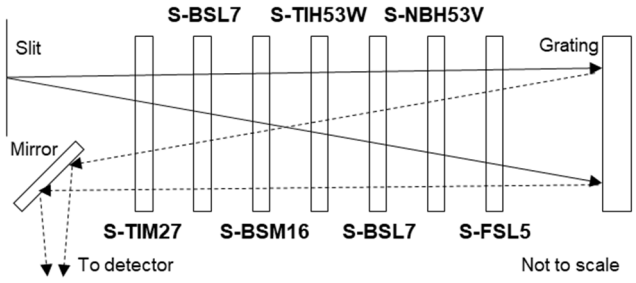

Fig. 1. Optical layout of our LIBS spectrometer.

Table 1. Glasses used in the LIBS spectrometer and previous studies on their resistance to radiation.

Type	n_d	Radiation effect study
S-TIM27	1.640	This study
S-LAM3	1.717	This study
S-TIH53W	1.847	This study
S-NBH53V	1.738	This study
S-BSL7	1.487	Nishino et al., 1998 [16]
S-FSL5	1.516	Topcon Corp.
S-BSM16	1.620	Topcon Corp.

and near-Earth primarily encounter proton radiation, glasses exhibit similar dose dependence to gamma-ray radiation [11]; therefore, we carried out the experiments using a ^{60}Co gamma-ray source.

The irradiation was conducted at the Takasaki Institute for Advanced Quantum Science. Radiation doses were selected based on estimates for the Martian Moons eXploration mission (MMX) [12]. Over the 5 years of the mission, ~100 Gy (10 krad) of proton radiation is anticipated, assuming a 2 mm thick Al cover equivalent to the thinnest part of a standard planetary instrument.

The optical glasses were irradiated with doses of 10–10,000 Gy (H_2O; 1–1,000 krad) using two different sources. On October 13, 2022, doses of 10, 20, 50, and 100 Gy were applied at a rate of 20 Gy/h. On September 26, 2022, doses of 300, 1,000, and 10,000 Gy were applied at a rate of 3,000 Gy/h. Dose levels were controlled by adjusting the distance from the radiation sources and monitored using a dose meter.

2.2. Analysis

The transmission spectra for the irradiated glass samples were measured using a UV/VIS spectrometer (U-4100, Hitachi) at Topcon, covering wavelengths of 200–1,200 nm with a resolution of 0.5 nm (Fig. 2). The accuracy and precision of the measurements were 0.3% and 0.1%, respectively.

Transmittance values were calculated from transmission values using the following equation, which accounts for reflection loss [13]:

$$T = (1 - R)^2 T_0 \quad (1)$$

where T is the measured transmission value, T_0 is the internal transmittance value, and R is the reflection loss coefficient given by:

$$R = \left(\frac{n_d - 1}{n_d + 1}\right)^2, \quad (2)$$

where n_d is the refractive index (Table 1). Previous studies have indicated that the glass transmittance can recover over time because of defect recombination in

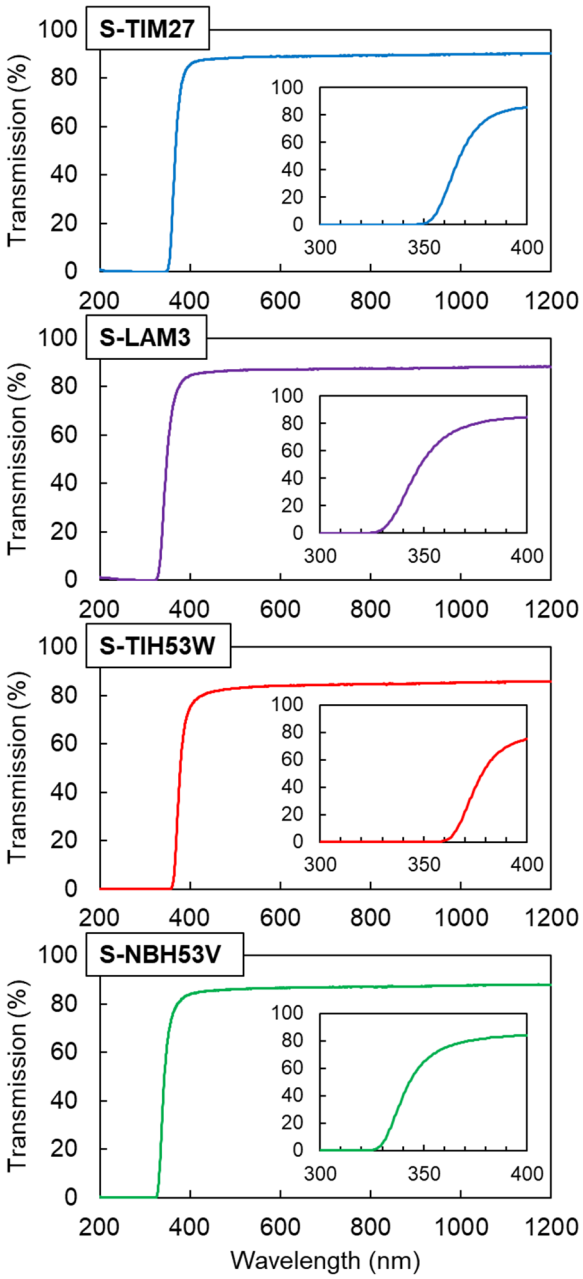

Fig. 2. Transmission spectra of the four studied glasses. Magnified figures show the wavelength range at which the transmissions decrease.

the glass [9,14,15,16]. To study the recovery dynamics, measurements were taken 1, 8, 15, 30, 91, 182, 273, and 365 days after irradiation. Earlier works used the thickness-normalized absorption coefficient, α (cm^{-1}), to analyze the recovery of transmittance in irradiated glasses. This coefficient is defined by the following equation [15,16]:

$$\alpha x = -\ln\left(\frac{T}{(1-R)^2}\right), \quad (3)$$

where x is the thickness of the glass (0.5 cm). We extended this approach to calculate the time-dependent absorption coefficients for each type of glass to characterize transmittance recovery.

3. Results

After gamma-ray irradiation, the transmittance of the glass materials decreased. The transmittances measured one day after irradiation are shown in Fig. 3. This reduction was evident across a broad range of wavelengths, from the short-wavelength transmission limit (~400 nm; Fig. 2) to ~1,000 nm. Although the magnitude of the decrease varied among different types of glass, it was larger at short wavelengths and less pronounced at long wavelengths, consistent with previous studies [9,14,15,16].

Figure 4 shows the temporal evolution in the transmittance of the four glasses irradiated with a 100 Gy dose. Although increases in transmittance were small, continuous recovery was observed in all glasses. Figure 5 shows the recovery of α at a wavelength of 400 nm. The time-dependent recovery of α can be described by the following equation [9]:

$$\alpha(t) = \alpha_\infty + A\exp(-kt), \quad (4)$$

where α_∞ is the recovered transmittance after an infinite time, k is the rate constant for recovery, and A is a scaling constant. Previous studies have identified two distinct phases in transmittance recovery: long-term (≥ 50 days) recovery due to the recombination of electrons and defects, which can be approximated by an exponential function; and short-term (≤ 50 days) recovery due to the recombination of defects with other defects, which follows second order of reaction [9]. These phases are influenced by irradiation conditions and glass composition [9].

To fit the data, data points were removed sequentially starting with the first following irradiation until the sum of the squares of the residuals fell below the measurement error. Consequently, the data collected 1–8 days after irradiation with a 10,000 Gy dose and the data from 1 day after irradiation with 300–1,000 Gy doses were excluded from the fitting procedure to better capture the long-term recovery. This is consistent with previous results that suggest that higher radiation doses lead to longer short-term recovery periods [9].

The α_∞ and k values at 400 nm obtained from the fits are listed in Table 2, along with the estimated recovery half-life, $t_{1/2}$ [$k^{-1}\ln(2)$]. The recovered transmittance, T_∞, was calculated using Equation 3, assuming a thickness of 0.5 cm. The calculated $t_{1/2}$ values were < 365 days, except for in S-NBH3V, suggesting that our transmittance measurements covered the recovery timescale adequately, although additional measurements may be needed to obtain more accurate recovery parameters for S-NBH3V.

Substantial decreases in T_∞ and increases in $t_{1/2}$ occur at doses > 300 Gy, except for in S-TIH53W. The recovery parameters at these higher doses better represent the long-term behavior, as the data points affected by the short-term recovery phase (1–8 days after irradiation) were not included in the fit.

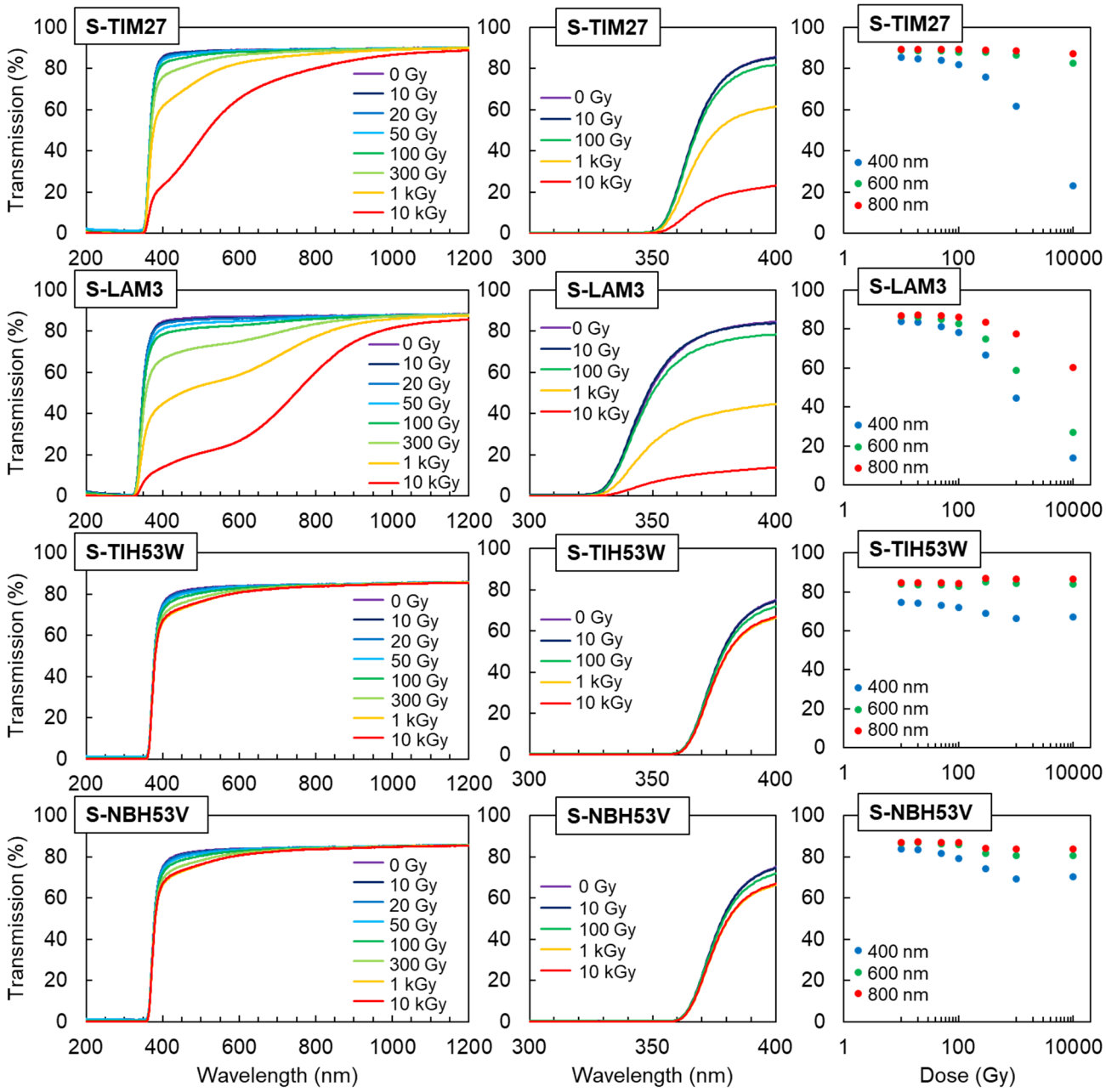

Fig. 3. Transmission spectra of glasses one day after gamma-ray irradiation. Left: Transmission spectra over the full wavelength range. Center: Spectra over the range of wavelengths where transmission decreases. For clarity, the spectra with doses of 20, 50, and 300 Gy are not shown. Right: Transmission values of glasses at wavelengths of 400, 600, and 800 nm one day after irradiation versus gamma-ray dose.

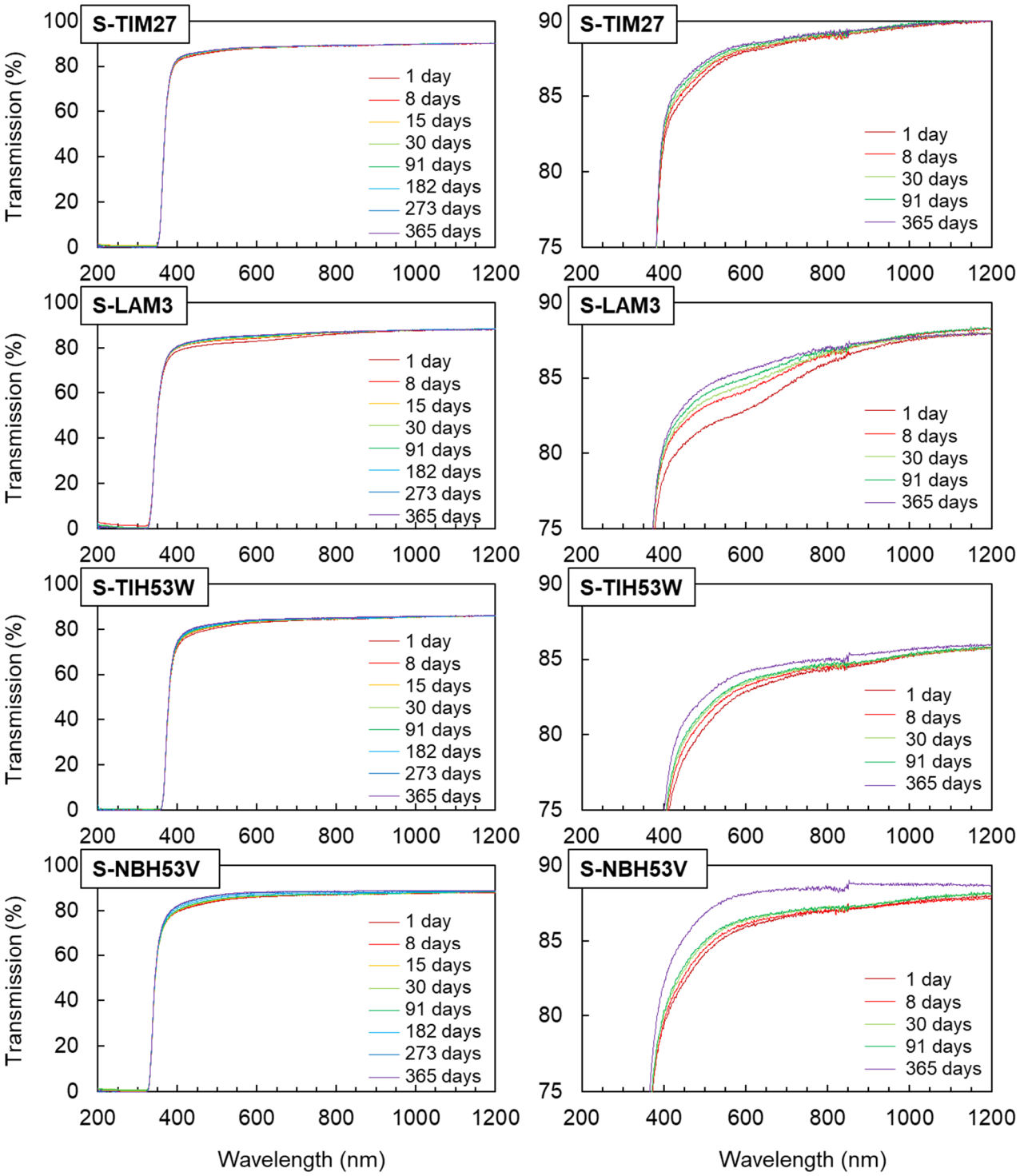

Fig. 4. Evolution of the transmission spectra of glasses irradiated with a 100 Gy dose. Left: Full range of wavelengths. Right: Spectra over the range of wavelengths with 75%–90% transmission, highlighting the variation. For clarity, spectra measured 15, 182, and 273 days after irradiation are not shown.

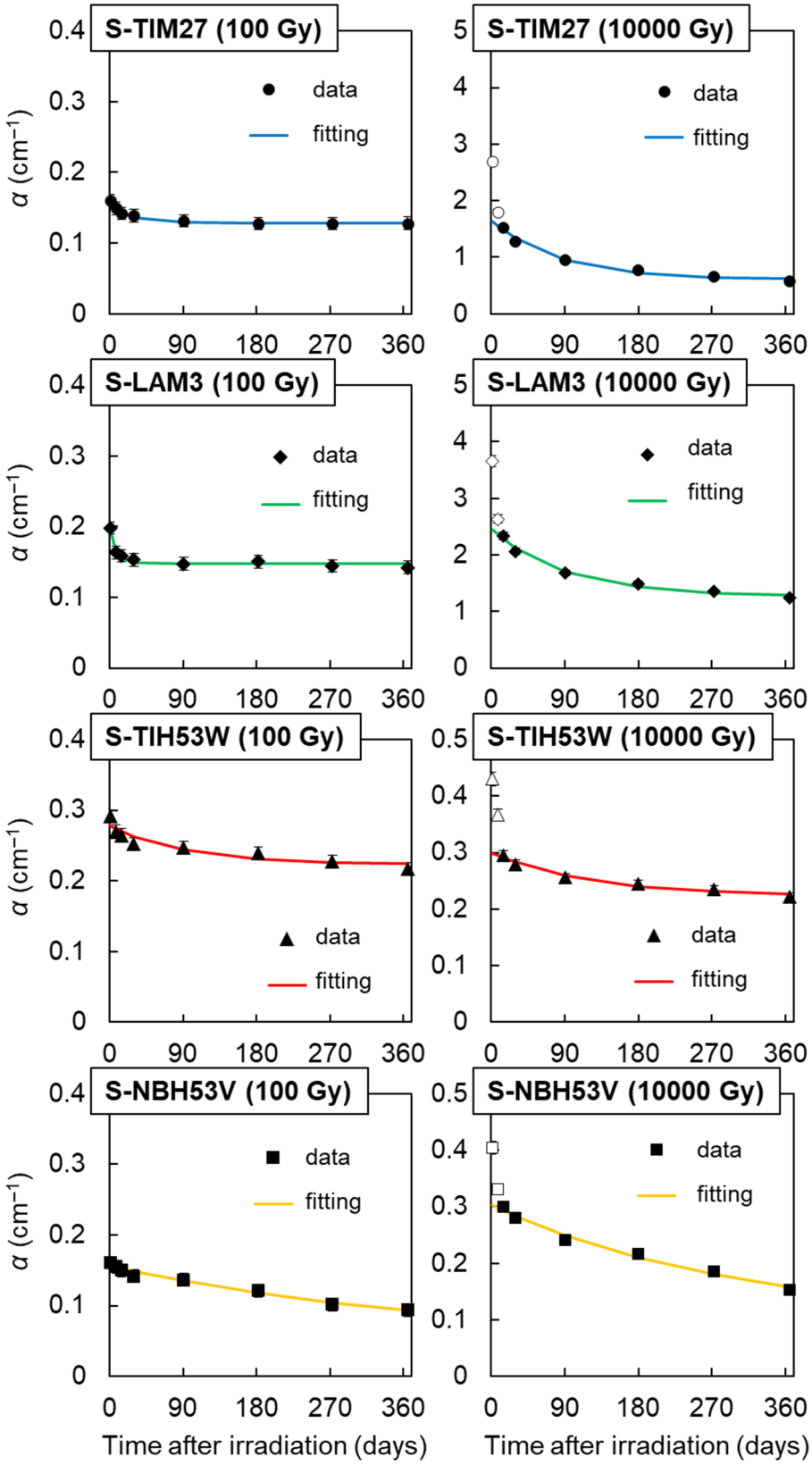

Fig. 5. Recovery of absorption coefficients of irradiated glasses at a wavelength of 400 nm. Left: Glasses irradiated with a 100 Gy dose. Right: Glasses irradiated with a 10,000 Gy dose. Black symbols are calculated absorption coefficients, and colored curves are least-square fits. In the right panels, data points corresponding to 1 and 8 days after irradiation, indicated by white symbols, were excluded from the fitting process (see Section 3). Error bars represent 1σ uncertainties in transmission measurements.

Table 2. Recovery parameters for irradiated glasses obtained from least-square fits.

	Dose (Gy)	α_∞ (cm^{-1})	T_∞ (%)	k (day^{-1})	$t_{1/2}$ (days)
S-TIM27	10	0.071	**85.5**	2.98×10^{-2}	23
	20	0.082	**85.1**	8.47×10^{-2}	8.2
	50	0.100	**84.3**	2.66×10^{-2}	27
	100	0.128	**83.1**	4.64×10^{-2}	15
	300	0.212	**79.7**	8.60×10^{-3}	81
	1000	0.377	**73.4**	1.10×10^{-2}	63
	10000	0.603	**65.5**	1.20×10^{-2}	58

	Dose (Gy)	α_∞ (cm^{-1})	T_∞ (%)	k (day^{-1})	$t_{1/2}$ (days)
S-LAM3	10	0.047	**84.6**	1.17×10^{-1}	5.9
	20	0.059	**84.0**	7.68×10^{-2}	9.0
	50	0.029	**82.3**	7.91×10^{-2}	8.8
	100	0.147	**80.4**	1.31×10^{-1}	5.3
	300	0.365	**72.1**	1.06×10^{-2}	65
	1000	0.792	**58.3**	1.20×10^{-2}	57
	10000	1.27	**45.8**	1.12×10^{-2}	62

	Dose (Gy)	α_∞ (cm^{-1})	T_∞ (%)	k (day^{-1})	$t_{1/2}$ (days)
S-TIH53W	10	0.178	**76.0**	9.50×10^{-3}	76
	20	0.185	**75.7**	5.22×10^{-3}	2.5×10^{2}
	50	0.206	**75.0**	1.39×10^{-2}	1.1×10^{2}
	100	0.223	**74.3**	1.11×10^{-2}	63
	300	0.251	**73.3**	8.74×10^{-3}	79
	1000	0.240	**73.7**	5.46×10^{-3}	1.3×10^{2}
	10000	0.222	**74.3**	8.15×10^{-3}	85

	Dose (Gy)	α_∞ (cm^{-1})	T_∞ (%)	k (day^{-1})	$t_{1/2}$ (days)
S-NBH53V	10	0.058	**86.0**	5.07×10^{-3}	1.4×10^{2}
	20	0.066	**86.0**	3.08×10^{-3}	2.2×10^{2}
	50	0.106	**86.0**	1.62×10^{-3}	4.3×10^{2}
	100	0.049	**83.9**	2.42×10^{-3}	2.9×10^{2}
	300	0.000	**86.0**	1.07×10^{-2}	6.5×10^{2}
	1000	0.112	**81.3**	2.04×10^{-3}	3.4×10^{2}
	10000	0.093	**82.1**	3.24×10^{-3}	2.1×10^{2}

4. Discussion

We evaluated the optical performance of our spectrometer when exposed to a total radiation dose of 100 Gy (10 krad) based on the results above. The decline in the transmittance of the glasses at a wavelength of 400 nm one day after being irradiated with this dose, excluding S-LAM3 (which is not used in the spectrometer), was 3.2%–4.7% (Fig. 3; Section 3).

Over time, the transmittance recovered. After 365 days, the transmittance loss was reduced to 1.2%–3.9% of the pre-irradiated value (Fig. 4). Based on the results of higher-dose experiments, the timescale of recovery was estimated to be 60–130 days, or longer for S-NBH53V. For a 100 Gy dose, the post-recovery transmittance values of S-TIM27, S-TIH53W, and S-NBH53V were estimated at 83.1%, 74.3%, and 83.9%, respectively (Table 2). Along the optical path of our spectrometer, these values correspond to a total transmission of 26.8%, 88.4% of the original unirradiated total transmission (30.4%), as light passes each lens twice as it travels from the slit to the detector. Similarly, relative total transmission values after a dose of 100 Gy were 84.0% at 390 nm, 83.7% at 380 nm, and 82.8% at 370 nm of those of the original unirradiated materials.

During planetary missions, significant radiation exposure typically occurs during specific events, including traversing Earth's radiation belts [17]. Therefore, the effective transmission during analyses on the target body is likely to be close to post-recovery values. Moreover, a 100 Gy dose is the maximum estimated for a 5-year mission to Mars. Given that the LIBS instrument would likely have more protection than a 2 mm thick aluminum cover, our estimates probably overstate the impact of radiation on the optical system. Note that our study is not intended to specifically estimate the degraded transmittance values but to assess whether the materials used in the spectrometer are resilient to the radiation expected in lunar and planetary exploration missions.

Our results indicate that the tested glasses can maintain at least 80% of their original transmittance at wavelengths ≥ 370 nm, which are required for detecting key elements comprising lunar materials (Section 1), when exposed to 100 Gy of radiation. The quantity of photons reaching the detector is influenced by the distance between a rock sample and the LIBS instrument. Since the photon flux is inversely proportional to the square of the distance, the decrease in transmittance to 80% is equivalent to a 10% decrease in the measurable distance range ($0.8 \approx 0.9^2$). Such a slight reduction would not significantly affect the sample selection criteria for a rover. Similarly, it would impose only a relatively minor constraint on the sample selection criteria for a lander. This confirms the resistance of these glass materials to radiation during their intended use in a LIBS instrument during planetary exploration missions and in other optical systems that use the studied materials.

5. Conclusions

We conducted gamma-ray irradiation tests on four glass materials that had not previously been investigated for the effects of radiation on transmittance. The experiments covered a range of doses from 10 to 10,000 Gy (1 to 1,000 krad), which includes the 100 Gy dose estimated for the MMX mission. The transmittances of the glasses were measured periodically from 1 to 365 days after irradiation. For a 100 Gy dose, an initial reduction in transmittance of 3.2%–4.7% at a wavelength of 400 nm was observed one day after irradiation. This decrease reduced to 1.2%–3.9% after 365 days, with estimated recovery timescales of 60–130 days, depending on the glass type.

In a LIBS spectrometer, the maximum signal loss due to radiation-induced browning relative to an unirradiated instrument would be < 20% at a wavelength of 370 nm, and smaller at wavelengths of > 370 nm. This suggests that the tested glass materials are resilient to the radiation expected during lunar and planetary exploration missions. This study provides

crucial data on the radiation resistance of these glasses, informing the design of optical instruments, including LIBS spectrometers, intended for use in space exploration missions.

Acknowledgments

This work was supported by Grants-in-Aid for Scientific Research from the Japan Society for the Promotion of Science (JSPS KAKENHI Grants JP22K20378, JP21H04515, and JP23H01225) and JAXA. We wish to thank Dr. Eri Tatsumi for her constructive comments, which improved the manuscript.

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JAXA Research and Development Report JAXA-RR-23-006E

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Edited and Published by: Japan Aerospace Exploration Agency
7-44-1 Jindaiji-higashimachi, Chofu-shi, Tokyo 182-8522 Japan
URL: https://www.jaxa.jp/
Date of Issue: February 14,2024
Produced by: Matsueda Printing Inc.