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Journal of Nuclear Materials 283–287 (2000) 898–902

journal of nuclear materials

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Study on the damaging process of silica by in-reactor luminescence

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Abstract

We have carried out in situ luminescence measurements of silica glasses in a fission reactor. In the in-reactor-luminescence (IRL) spectra, the 300-nm band was observed for all the samples and its intensity stayed constant during irradiation. For low-OH fused silica glass, the 400-nm IRL band was also observed and reduced rapidly with irradiation, while for high-OH fused and synthesized silica glasses, the 450-nm IRL band grew slowly. The comparison with photoluminescence (PL) and electron spin resonance (ESR) spectra showed that the decrease of the 400-nm IRL band reflects the transition of $B_{2\beta}$ center to E' center by electron excitation by γ-rays, while the growth of the 450-nm IRL band related to defect formation from neutron irradiation. However, single crystal silica showed only a 300-nm IRL band, suggesting that the damaging processes are influenced by the local structure around defects as well as the OH content in silica. © 2000 Elsevier Science B.V. All rights reserved.

1. Introduction

Recently, silica has attracted attention as a material for optical windows, insulators and optical fibers in nuclear environments such as fusion and fission reactors. However, the optical and electrical properties of the silica are strongly influenced by the defects which are easily produced by energetic photons (UV light, X-ray or γ-ray) and/or particles (ions, electrons or neutrons) [1–4]. Many studies have been done to understand the defects in silica by the optical, electron spin resonance (ESR) and microscopic techniques. They have provided important information about the chemical and electronic state and/or the stability of the defects in silica. However, the detailed mechanism of the defect formation is still unclear, because most of the previous studies have been done for silica after irradiation. In situ observation of silica under irradiation is required to get the information about the dynamic damaging processes. Moreover, the defect formation process is influenced by the manufacturing history, the structure and the OH content of silica [5,6].

In the present study, we have carried out in situ measurements of the luminescence from silica (both glasses and a single crystal) under in-reactor irradiation in order to discuss the dynamic irradiation effects on silica. The out-of-pile measurements of the photoluminescence and ESR have also been performed to obtain detailed information about the defects produced by the reactor irradiation.

2. Experimental

Silica samples used in this study were a low-OH fused silica glass (T-2030: OH < 1 ppm), a high-OH fused silica glass (T-1030: OH 200 ppm) and a high-OH synthesized silica glass (T-4040: OH 800 ppm). All of these samples

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PII: S0022-3115(00)00160-4

were 13 mm in diameter and 2 mm thick produced by Toshiba Ceramics, Japan. Nominal impurity levels of them are described elsewhere. A single crystal silica with dimensions of 10 × 10 × 1 mm^3 produced by Tateho Kagaku, Japan, was also studied for comparison.

In-reactor-luminescence (IRL) measurements have been performed using the experimental reactor YAYOI at the University of Tokyo. The luminescence from the samples during irradiation in the reactor core was transmitted to a spectrometer by a light guiding tube and an optical fiber. The luminescence of the light guiding tube itself was not observed. The detecting efficiency (including reflectivity in the guiding tube and optical fiber transmission) was ca. 95% in the region from 250 to 800 nm, however, it was remarkably reduced in the region less than 250 nm, as the use of the optical fiber. The average power of YAYOI was 0.5 kW (neutron flux of 2×10^{15} n/m^2 s) or 1.5 kW (neutron flux of 6×10^{15} n/m^2 s), and the average neutron energy was 1.3 MeV and the γ-ray dose rates of both neutron fluxes were about 3.0 kGy/h. The irradiation temperature was below 323 K. The details of the IRL measurements are described elsewhere [7].

A γ-ray irradiation was performed at room temperature with a dose rate of 11.2 kGy/h using ^{60}Co γ-ray sources at the Research Reactor Institute, Kyoto University.

Photoluminescence (PL) and ESR spectra for irradiated samples were measured at room temperature by using a Hitachi F-4500 spectrophotometer and a JEOL (JES-TE 200) ESR spectrometer operating at *X*-band frequency, respectively.

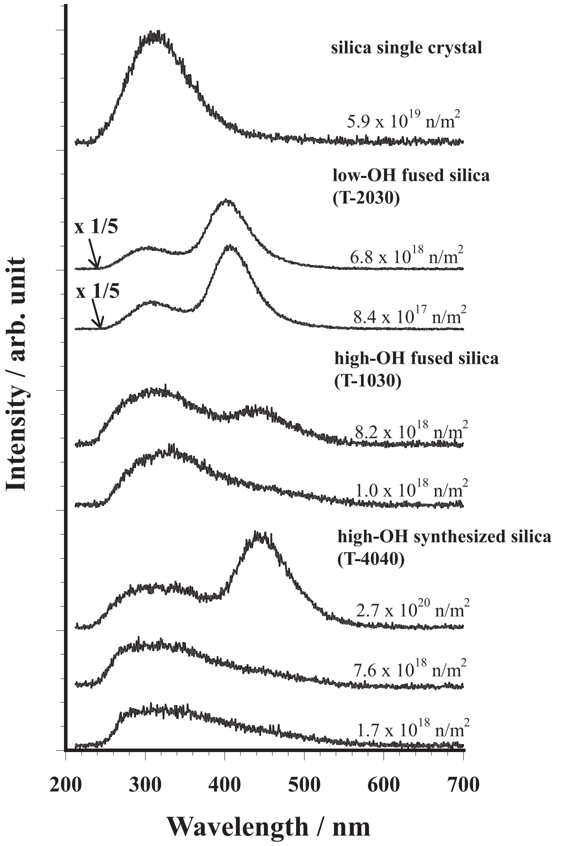

Fig. 1. Luminescence spectra from silica during irradiation in the reactor core.

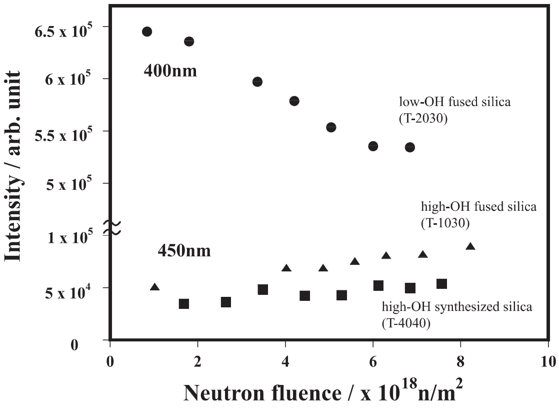

Fig. 2. The variations of the intensity of the band at 400 or 450 nm in the IRL spectra with the neutron fluence.

3. Results

3.1. *IRL from silica*

Fig. 1 shows the IRL for three silica glasses and a single crystal silica. Each sample shows that the spectra fundamentally consist of two broad bands at 300 nm and 400 or 450 nm. The 300-nm IRL band appeared for all samples and its intensity kept constant during irradiation. The 400-nm IRL band was observed only for the low-OH fused silica (T-2030) and decreased with irradiation dose, while the 450-nm IRL band was seen for high-OH fused and synthesized silica (T-1030 and T-4040) and increased with irradiation dose. There was no detectable band in single crystal silica except for the 300 nm IRL band even after prolonged irradiation.

In Fig. 2, the intensities of the 400- and 450-nm IRL bands are plotted against the neutron fluence. The intensity of the 400-nm IRL band for the low-OH fused silica decreased rapidly with neutron fluence but remained much stronger than that for the 450-nm IRL band for the high-OH fused and for synthesized silica, which gradually grew. Therefore, the 400-nm IRL band can be attributed to intrinsic defects in low-OH fused silica, while the 450-nm IRL band can be attributed to new defects produced in the high-OH fused and synthesized silica glasses by in-reactor irradiation.

3.2. Photoluminescence (PL) spectra of silica before and after in-reactor irradiation

Fig. 3 shows PL spectra excited by 240 nm photon for the low-OH fused silica (T-2030), the high-OH synthesized silica (T-4040) and the single crystal silica before and after irradiation in the fission reactor. Similar to the IRL spectra, the PL spectra had two broad bands at ca 300 and 400 or 450 nm. Two PL bands at 300 and 400 nm were observed for unirradiated low-OH fused silica. After in-reactor irradiation, the 400 nm PL band progressively decreased. Anedda et al. and Skuja et al. assigned these PL bands to the emission of the $B_{2\beta}$ type oxygen-deficient center (two-coordinated silicon, O–Si–O) [6,8]. These results suggest that $B_{2\beta}$ center is the intrinsic defect in the low-OH fused silica and the defect decreased with irradiation.

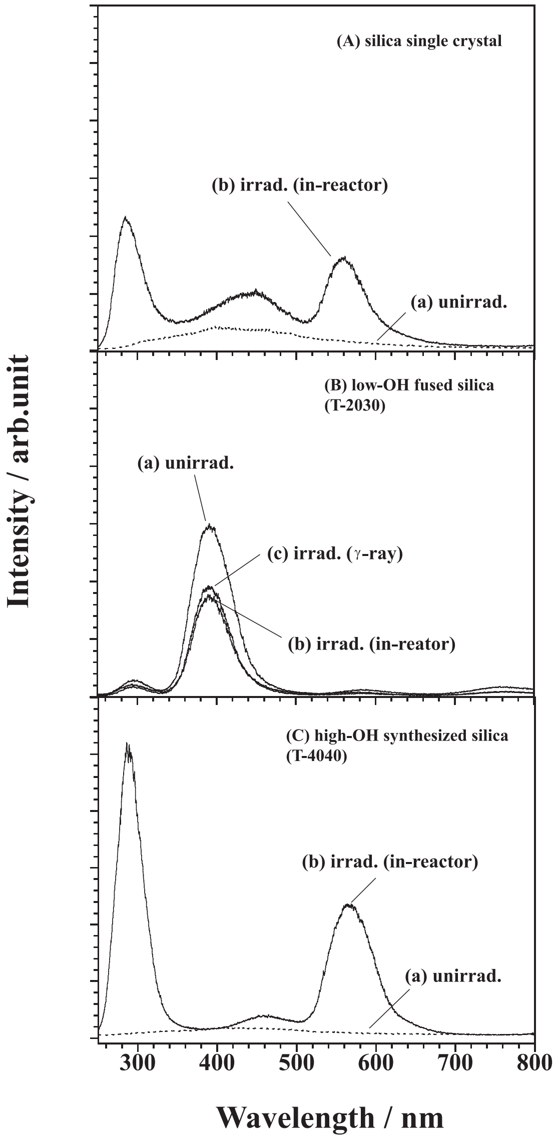

Fig. 3. PL emission spectra of silica excited by 240 nm photon: (A) an unirradiated single crystal silica (a) and the reactor-irradiated one (neutron fluence is 6.0×10^{19} n/m^2) (b); (B) an unirradiated low-OH fused silica (a), the reactor-irradiated one (neutron fluence is 8.5×10^{18} n/m^2) (b) and the γ-irradiated one (γ-ray dose is 11.2 kGy) (c); (C) an unirradiated high-OH synthesized silica (a) and the reactor-irradiated one (neutron fluence is 2.7×10^{20} n/m^2) (b).

For the high-OH synthesized silica and the single crystal silica, no remarkable PL spectra were observed for the unirradiated samples. On the other hand, those of the irradiated samples had double PL peaks at 290 and 450 nm (the peak at 580 nm is mostly owing to the second-order diffraction of the peak at 290 nm), which are characteristic of the $B_{2\alpha}$ center (a neutral oxygen vacancy, $\equiv$Si:Si$\equiv$) [6,8].

For the in-reactor irradiation, the effect of γ-rays is superposed on that of neutrons. We have made γ-ray irradiations in ^{60}Co γ-ray source (γ-ray dose; 11.2 kGy) of low-OH fused silica glass, high-OH synthesized silica glass and a single crystal silica, and measured PL spectra excited at 240 nm. Although the PL spectra of the high-OH silica glass and the single crystal silica after the γ-ray irradiation were almost the same as those of their unirradiated samples, the drastic reduction of the 400 nm PL band was found only for the γ-ray irradiated low-OH fused silica.

3.3. ESR spectra

We also measured the ESR spectra of the low-OH fused silica before and after irradiation. Although the ESR spectrum of the unirradiated material did not exhibit remarkable signals, the characteristic ESR signals were observed for the sample after irradiation. Fig. 4 shows the ESR spectra of the low-OH fused silica glasses irradiated in the reactor (neutron fluence; 3.2×10^{19} n/m^2) and in the ^{60}Co γ-ray sources (γ-ray dose; 11.2 kGy). Based on the ESR spectra and *g* values reported for silica [9,10], both spectra are assigned to the E$'$ center. This result strongly indicates that E$'$ center is preferentially formed in low-OH fused silica mainly by γ-ray irradiation.

4. Discussion

4.1. The origin of the 300-nm band of the in-reactor luminescence

As shown in Table 1, the 300-nm IRL band which appeared in all samples did not change with the irradiation. On the other hand, all PL bands at 290 or 300 nm changed with the irradiation. This means that the

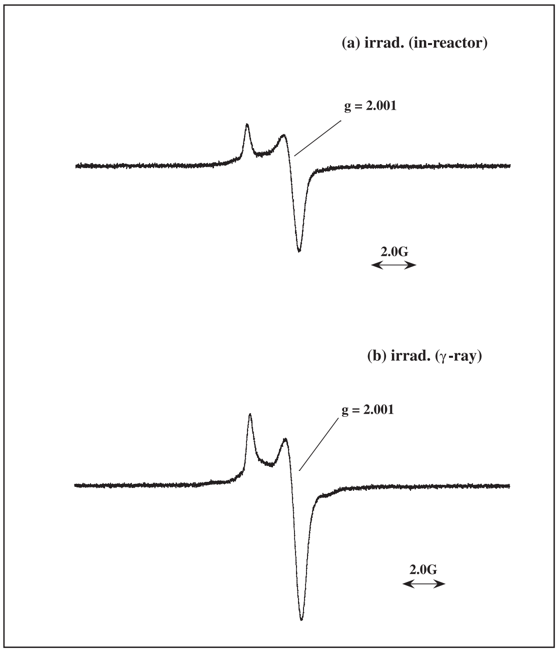

Fig. 4. ESR spectra of the in-reactor irradiated low-OH fused silica (neutron fluence is 8.5×10^{18} n/m^2) (a) and the γ-irradiated one (γ-dose is 11.2 kGy) (b).

300-nm IRL band cannot be correlated to the B_2 centers. Mogle et al. [11] have attributed their 288 nm emission in their electroluminescence study of silica to the E' center, which was confirmed by its characteristic ESR signal. However we cannot attribute the 300 nm band of the IRL to the E' center, because no ESR signals were observed before irradiation in all of the silica used in this study. Therefore, the 300-nm IRL band may be due to exiton or Cerenkov radiation. Shikama et al. [12] attributed the IRL from optical fibers in the Japan Material Testing Reactor (JMTR) to Cerenkov radiation, the intensity of which is inversely proportional to the square of wavelength. However, as seen in Fig. 1, the IRL emission peaked at 300 nm, which may exclude the Cerenkov continuum. Therefore, in the present study, the 300-nm IRL band is likely due to exitons.

4.2. The origin of the 400- or 450-nm band of the in-reactor luminescence

The 400-nm IRL band for the low-OH fused silica decreased rapidly with reactor irradiation. This is parallel to the decrease of $B_{2\beta}$ center that appeared as the 400-nm PL band for the same samples irradiated in the reactor or by γ-ray. On the contrary, the ESR signal assigned as E' center appeared and increased with the irradiation dose. Ishii et al. and Amossov et al. [13,14] indicated that B_2 centers are easily transformed to E' centers by electron excitation on the basis of their UV photon irradiation studies. Thus the intrinsic $B_{2\beta}$ center in the unirradiated low-OH fused silica is very likely transformed to E' centers by γ-ray irradiation (through the electron excitation of γ-rays) in reactor.

Different from the 400-nm IRL band of the low-OH fused silica, the 450-nm IRL band for the high-OH fused and synthesized silica glasses increased gradually with irradiation dose. In the PL spectra of the irradiated synthesized silica, the weak band at 450 nm, which is assigned to $B_{2\alpha}$ center, appeared. Therefore, the 450 nm IRL band is likely attributed to the $B_{2\alpha}$ center. Because the γ-irradiated high-OH synthesized silica hardly changed its PL spectra (not shown here), the increase of the $B_{2\alpha}$ centers by the reactor irradiation should be attributed to atomic displacement by neutron irradiation. Thus we conclude that silica glasses are subjected to two different damaging processes by reactor irradiation; i.e., one is a fast process in which the intrinsic $B_{2\beta}$ center is transformed into an E' center through the electron excitation by γ-ray; and the other is a rather slow process in which extrinsic oxygen deficiencies corresponding to $B_{2\alpha}$ centers are produced by the atomic displacement by neutron irradiation.

In the present study, $B_{2\alpha}B_2$ formation by irradiation was appreciable in the fused and synthesized silica glasses with high-OH contents. Therefore, the existence of OH seems to be the promoter of the defect formation by atomic displacement. Nevertheless, the IRL intensities in these glasses were much weaker (by a factor of about 5) than those of the low-OH fused silica; in other words, the number of intrinsic $B_{2\beta}$ defects were much smaller in the former than in the latter. This means the

Table 1
Results obtained from IRL, PL and ESR spectra[a]

	IRL			PL		ESR
	300 nm	400 nm	450 nm	300 nm, 400 nm	290 nm, 450 nm	
High-OH fused silica	→	×	↗	–	–	–
Low-OH fused silica	→	↘	×	↘	×	↗
High-OH synthesized silica	→	×	↗	×	↗	–
Silica single crystal	→	×	×	×	↗	–
Assignment		$B_{2\beta}$	$B_{2\alpha}$	$B_{2\beta}$	$B_{2\alpha}$	E'

[a] Intensity changes by the irradiation: → stay constant, ↗ increase, ↘ decrease, × not observed, – not measured.

original structure of silica glasses should be quite different with different OH contents.

From crystallographic consideration, it is reasonable that the single crystal silica is the most resistant to the displacement damage because of its strict tetrahedral bonding SiO_4. Correspondingly it showed the least IRL intensity in the 400–450 nm region compared to the other three silica glasses. Nevertheless the irradiation level of 6.0×10^{19} n/m^2 gave $B_{2\alpha}$ PL emission in a single crystal silica, i.e., some defects should be produced by the irradiation. This means the IRL emission is not simply caused by electron excitation by γ-rays. Because the γ-ray dose in the reactor is as high enough to give rise to radiation induced conductivity (RIC) [15], other electron excitation and de-excitation paths than luminescence might be present. If this happens, the OH content may play some role in the nonemissive de-excitation. In order to investigate the de-excitation process, dynamic measurement, such as lifetime measurements of the IRL and PL are necessary.

Another concern is the assignment of defect centers and associated structures. Although the simultaneous appearances of 290- and 450-nm bands in PL excited by 240 nm photons were used as evidence for the existence of $B_{2\alpha}$ centers, their intensity ratio was neither constant nor the same for different silica samples (see Fig. 3(A) and (C)). This suggests the existence of defect centers other than $B_{2\alpha}$. Unfortunately, one cannot directly see the chains of SiO_4 tetrahedra in amorphous glass structure, so there is no clear evidence for the previous assignment of the defect centers and associated atomic structures. From the present results, one may say the existence of OH suppresses the appearance of intrinsic $B_{2\beta}$ centers in silica glass, which is of course meaningless without a realistic model for the role of OH in the SiO_4 network. Proper use of new techniques, like EXAFS and EXELFS that are suitable to study the ordering over intermediate distance, will show the differences of structure among amorphous materials (especially the difference in the angle of the Si–O–Si). These are important subjects in our next study.

5. Conclusion

We have carried out in situ measurements of luminescence from various types of silica samples under fission reactor irradiation. The origin of the luminescence was very likely related to oxygen deficiency. Based on the analysis of the IRL, PL and ESR spectra, silica glasses have two dynamic damaging processes. One is a fast process where the intrinsic $B_{2\beta}$ center is transformed into an E' center through electron excitation by γ-ray irradiation, and the other is a slower defect formation process of atomic displacement by neutron irradiation. However, IRL emission was not simply explained by the electron excitation by γ-ray irradiation at the oxygen deficient centers, i.e., the OH content and the structure of the silica samples have some important roles on the damaging process in silica. These factors should be further investigated to understand the origin of the IRL, i.e., the dynamic damaging effects in silica samples.

Acknowledgements

The authors are grateful to Professor Tadashi Hattori of Department of Applied Chemistry, Graduate School of Engineering, Nagoya University for his co-operation in the PL measurements.

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