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In situ luminescence and optical absorption measurements of silica in reactor core

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Abstract

In situ optical measurements of silica glasses under in-reactor and γ-ray irradiation have been carried out. Two types of emission bands attributed to $B_{2\alpha}$ and $B_{2\beta}$ oxygen deficient centers were clearly distinguished from their different behavior with irradiation time. The $B_{2\alpha}$ center was created mainly by the atomic displacement effect due to neutron irradiation. On the other hand, the $B_{2\beta}$ center, which has two origins, intrinsic and newly formed (from its precursor states), was transformed to E′ centers through the electronic excitation effect of γ-ray irradiation. The present in situ experiments also showed the possibility that the $B_{2\beta}$ center can also be created by the displacement process caused by Compton electrons under γ-ray irradiation.

1. Introduction

Silica glasses are now widely used as optical windows, insulators and optical fibers under fission environments [1–6] and will be used in future *D–T* burning fusion apparatus. The optical and electrical properties of the silica, however, are easily degraded by point defects or radiation damages from the irradiation of high-energy ions, electrons, neutrons and γ-rays. Many studies have provided important information about the chemical and electric states of the defects in silica. Nevertheless, the details of the defect structures and the defect formation mechanisms are still unclear. Moreover, the effects of ionizing radiation (or electron excitation) and atomic displacement during the damaging process are not well distinguished, because most of the damage studies have been performed using post-irradiation tests. Since the relaxation (or de-excitation) time of excited electrons is very short, post-irradiation tests can give only 'traces' or 'results', but not 'processes'. This have motivated us to perform in situ measurements of luminescence and optical absorption for silica glasses in-reactor and/or under γ-ray irradiation. The main objective of this report is to obtain a clear understanding of the damaging processes in silica glasses by distinguishing between ionization and displacement effects.

2. Experimental

Three types of samples were used in the present study: 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 manufactured by Toshiba Ceramics, Japan. They were cut into circular disks of 13 mm diameter and 2 mm thickness. Nominal metal impurities

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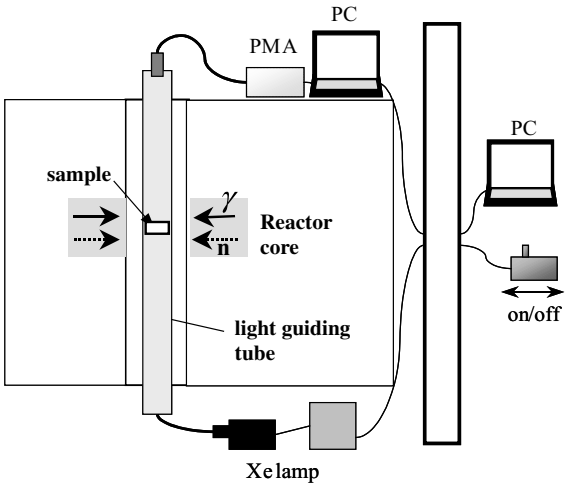

Fig. 1. The measurement system for the IRL and optical absorption of silica glass irradiated in the reactor core.

were Al (<8 ppm), Fe, Na and K (<1 ppm), which had no influence on the present optical measurements.

The in-reactor luminescence (IRL) and optical absorption spectra of the samples were measured in the nuclear reactor YAYOI at the University of Tokyo, as illustrated in Fig. 1. The luminescence of the sample irradiated in the reactor core was transmitted to a spectrometer (PMA-11, HAMAMATSU) away from the core by an aluminum light guiding tube and an optical fiber, avoiding the direct influence of background radiations on a photon detecting system. The luminescence of the light guiding tube itself was not measured. Due to the poor transmittance of the optical fiber for photons above 5 eV, the photon detecting efficiency above 5 eV was very low.

For the measurement of the optical absorption of the silica glass at the reactor core, the light from a Xe lamp was introduced through the optical fiber and the light guiding tube as shown in Fig. 1. The Xe lamp was controlled remotely and switched-on only for the optical absorption measurements so that the UV light irradiation from the Xe lamp did not disturb the luminescence measurements.

YAYOI was operated with a power of 0.5 or 1.5 kW (the neutron flux was about 2×10^{15} n/m^2 s and 6×10^{15} n/m^2 s, respectively) with an average neutron energy of 1.3 MeV and γ-ray dose-rate about 3 kGy/h [7]. The irradiation temperature was ambient but kept below 323 K because of the small output power of the reactor.

The luminescence measurements from the silica glass under the γ-ray irradiation were carried out using the ^{60}Co source at Nagoya university with the dose-rate at about 5.6 kGy/h for the silica.

3. Results

Fig. 2 compares the IRL spectra for the three types of silica glasses. Two broad bands at 4.2 eV and at 3.1 or 2.7 eV are dominant in the IRL spectra of all samples. Similar luminescence spectra have been reported for silica glasses under ion or electron irradiation, and are attributed to exciton and/or some oxygen deficient centers caused by electron excitations during the irradiation [8–10]. In the present study, the 4.2 eV IRL band, which appeared for all samples and did not change during the irradiation, probably originated from exciton or Cerenkov radiation [10,11], and will not be discussed.

The 3.1 and 2.7 eV emission bands were clearly distinguished from their different behavior with the irradiation time. In the IRL spectra (Fig. 2), the 3.1 eV band was observed only for the low-OH fused silica (T-2030) and the band intensity decreased with the irradiation dose but kept much stronger intensity than that of the 2.7 eV IRL band. The 2.7 eV band was seen for high-OH fused and synthesized silica (T-1030 and T-4040) and increased gradually with neutron fluence as shown in Fig. 3.

Fig. 4(a) shows the γ-ray induced luminescence spectrum of a low-OH fused silica glass (T-2030). Two pronounced bands at 4.2 and 3.1 eV first appeared, which is parallel to the result of the IRL bands of the

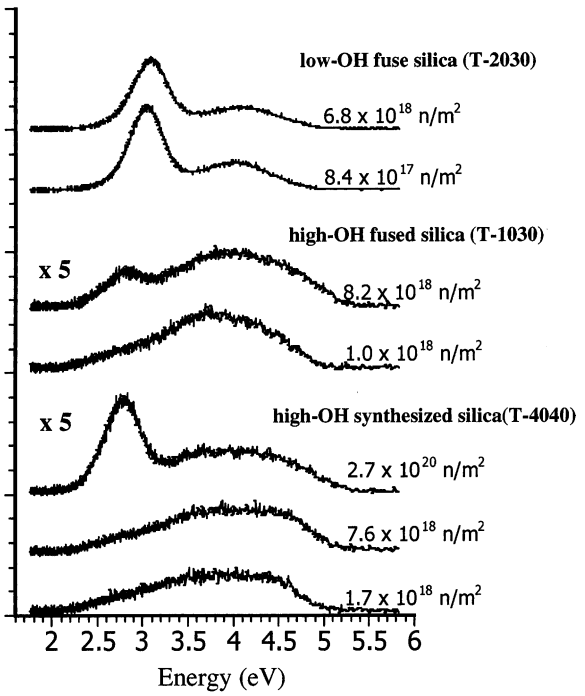

Fig. 2. Luminescence spectra from silica glasses during irradiation in the reactor core.

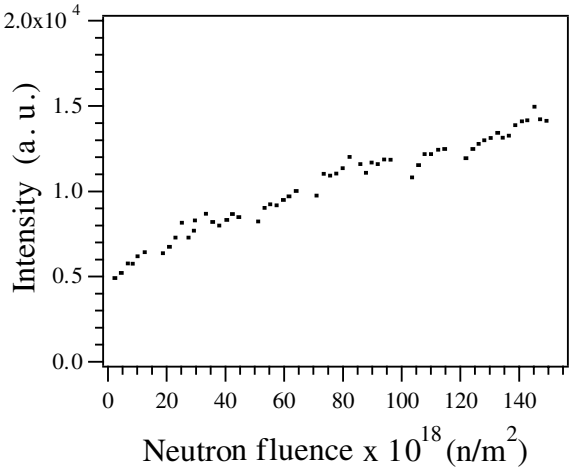

Fig. 3. The variation of the intensity of the band at 2.7 eV in the IRL spectra of the high-OH synthesized silica glass (T-4040) with the neutron fluence.

same type of sample. The intensity of the 3.1 eV band increased rapidly in the early stage of the irradiation and then turned to a gradual decrease for prolonged irradiation (Fig. 4(b)).

Different from the IRL, the γ-ray induced luminescence spectrum of a high-OH synthesized silica glass (T-4040) did not produce the 2.7 eV band even after prolonged γ-ray irradiation.

4. Discussion

4.1. The origins of two emission bands

In our separate out-of-pile optical measurements, an unirradiated low-OH fused silica glass (T-2030) showed the optical absorption band at ≈5.0 eV and the corresponding photoluminescence (PL) band at 3.1 eV. On the other hand, no prominent absorption and PL bands

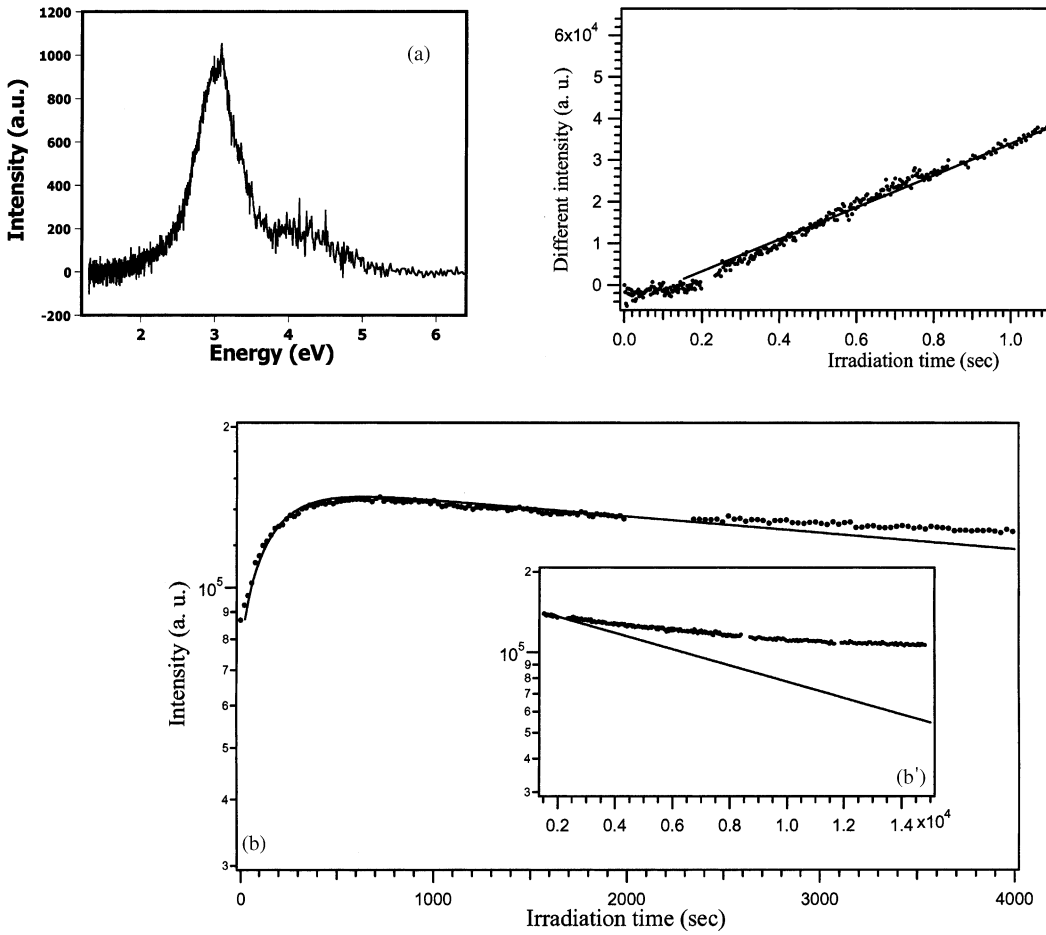

Fig. 4. (a) γ-ray induced luminescence spectrum of a low-OH fused silica glass, (b) and b′ (inset) time sequence of luminescence intensity of the 3.1 eV band under γ-ray irradiation (the dotted curve). The curve-fitting result is also shown with the solid curve. (c) The variation of the difference between the experimental data and the curve-fitting data with the γ-ray irradiation time.

were observed for an unirradiated high-OH synthesized silica glass (T-4040), while the optical absorption band at ≈5.0 eV and the 2.7 eV PL band could be seen for this high-OH silica glass after the in-reactor irradiation [12]. Tohmon et al. [13] reported the existence of two B_2 bands excited at around 5.1 eV: the $B_{2\alpha}$ (≡ Si:Si ≡) and $B_{2\beta}$ (O–Si–O) oxygen deficiencies. It is also well known that the PL emission band at 2.7 eV is attributed to the $B_{2\alpha}$ centers while $B_{2\beta}$ centers generate the 3.1 eV band [14–17].

Thus, we can assign the 3.1 eV emission band observed for the low-OH fused silica glass as $B_{2\beta}$ centers. Since the 3.1 eV emission band clearly appeared in the early stage of both in-reactor and γ-ray irradiations (Figs. 2 and 4(a)), a certain amount of $B_{2\beta}$ centers must have existed in this sample. This should be distinguished as intrinsic $B_{2\beta}$ centers, as opposed to extrinsic $B_{2\beta}$ centers.

The 2.7 eV emission band observed for the high-OH synthesized silica glass can be attributed to $B_{2\alpha}$ centers. Thus, we have observed in silica glasses two types of oxygen deficient centers, $B_{2\alpha}$ and $B_{2\beta}$.

4.2. The formation process of $B_{2\alpha}$ centers in the high-OH synthesized silica glass

In the IRL spectra of the high-OH synthesized silica glass, the band attributed to the $B_{2\alpha}$ center (at 2.7 eV) was observed and its intensity increased gradually with the in-reactor irradiation time. Moreover, in the in situ optical absorption measurements of this sample, the absorption band at ≈5 eV assigned to a B_2 center appeared and grew with increasing irradiation time (Fig. 5). These results indicate that the $B_{2\alpha}$ centers were created in the high-OH synthesized silica glass by the in-reactor irradiation.

On the other hand, the γ-ray induced luminescence spectrum of this sample did not show the $B_{2\alpha}$ emission band. Thus we can conclude that the creation of the $B_{2\alpha}$ centers were mainly due to the atomic displacement effect of neutrons in the reactor. This is confirmed by the good linear relationship between the luminescence intensity of the $B_{2\alpha}$ center (at 2.7 eV) and the neutron fluence as shown in Fig. 3.

4.3. The transformation and formation processes of the $B_{2\beta}$ centers in the low-OH fused silica glass

As shown in Fig. 4(b), the intensity changes of the $B_{2\beta}$ (3.1 eV) band observed for the low-OH fused silica glass suggested the transformation process of $B_{2\beta}$ centers during γ-ray irradiation. The time sequence of the $B_{2\beta}$ luminescence intensity in Fig. 4(b) can be divided into different regions by the irradiation time (t); (1) the initial increase ($0 < t < 500$), (2) the following gradual decay ($500 < t < 2500$) and (3) nearly saturation ($2500 < t$).

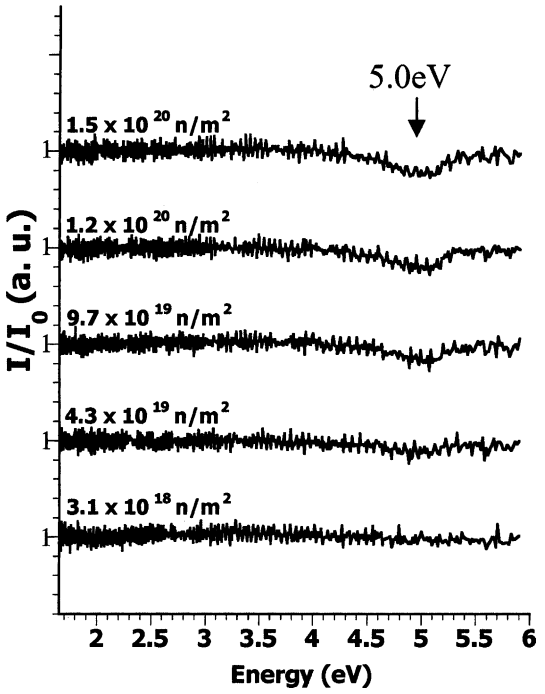

Fig. 5. The variation of the relative optical transmittance of a high-OH synthesized silica glass (T-4040) with the neutron fluence. I_0 and I are the transmitted UV–Vis light intensities for the unirradiated and the in-reactor irradiated silica glass, respectively.

Now we can attribute the initial increase to the conversion from the precursor states into $B_{2\beta}$ centers [18,19], and the following decay to the transformation of $B_{2\beta}$ centers to other types of oxygen deficiencies like E′ centers [20–22], because our separate ESR measurements clearly indicated the generation of E′ centers after the γ-ray irradiation [12].

Accordingly, we can make the following kinetic equations for the processes; (i) precursor → $B_{2\beta}$, and (ii) $B_{2\beta}$(precursor origin) → E′:

$$dN_{pr}/dt = -\sigma_{pr} D N_{pr}, \quad (1)$$

$$dN_{B_{2\beta}}/dt = \sigma_{pr} D N_{pr} - \sigma_{B_{2\beta}} D N_{B_{2\beta}}, \quad (2)$$

where N_{pr} and $N_{B_{2\beta}}$ are the numbers of the precursor and $B_{2\beta}$ center, respectively, σ_{pr} and $\sigma_{B_{2\beta}}$ the reaction coefficients, D the absorbed dose rate (Gy/s = J/kgs) of γ-ray, and t(s) the γ-ray irradiation time. Surprisingly, Eq. (2) fits the experimental data very well up to 2500 s as shown in Fig. 4(b). The fitting curve does not pass zero in the $t = 0$ s, confirming the presence of the intrinsic $B_{2\beta}$ centers in the low-OH fused silica glass.

In this kinetic model, however, the deviation becomes larger for prolonged irradiation time, which indicates the presence of a third process under the γ-ray

irradiation. When this deviation is replotted against the irradiation time as shown in Fig. 4(c), the increment shows a very good linear relationship with irradiation time. This indicates that new $B_{2\beta}$ centers seem to be produced by γ-ray irradiation. The above discussion (Eqs. (1) and (2)) is based on the processes caused mainly by electronic excitation processes (ionizing effect) under γ-ray irradiation [6,12]. On the other hand, this new $B_{2\beta}$ formation is probably caused by the displacement effect of the primary (Compton) or high energy electrons and photons which are generated in the low-OH fused silica glass by γ-ray irradiation.

Under in-reactor irradiation, similar defect formation processes should be added to the displacement effect of neutron irradiation. Actually, the intensity of the $B_{2\beta}$ emission band also exhibited a very slow decay for prolonged in-reactor irradiation. Unfortunately, we cannot distinguish between the displacement effects of the neutrons and the Compton electrons, but we expect that the latter effect would be much less than the former effect.

5. Conclusion

In the present study, in situ optical observations of silica glasses under in-reactor and γ-ray irradiations have been carried out, in order to study their damaging processes. Two types of $B_{2\alpha}$ and $B_{2\beta}$ oxygen deficient centers were observed, and these were clearly distinguished from their different behavior with the irradiation time.

In the IRL spectra of the high-OH synthesized silica glass, the intensity of the 2.7 eV band, attributed to $B_{2\alpha}$ centers, increased almost linearly with neutron fluence. Since no increase of the $B_{2\alpha}$ emission was observed in the γ-ray induced luminescence spectra, we concluded that the formation of the $B_{2\alpha}$ centers was caused mainly by the atomic displacement effect of neutron irradiation.

In the γ-ray induced luminescence spectra of the low-OH fused silica glass, the intensity of the $B_{2\beta}$ emission band increased rapidly in the early stage of the γ-ray irradiation and then turned to a gradual decrease for prolonged irradiation. The initial increase is attributed to the conversion of precursor states to the $B_{2\beta}$ centers, and the following decay to the transformation of $B_{2\beta}$ to E' centers by γ-ray irradiation. These processes are expected to occur through the electron excitation effect (ionizing radiation effect) of γ-rays. In addition to these processes, the kinetic model exhibited other processes induced by γ-ray radiation, in which new $B_{2\beta}$ centers were produced by the displacement effect of the primary (Compton) or high energy electrons and photons.

Thus, the present in situ optical measurements enabled us to understand quantitatively two dynamic damaging processes (defects formation and transformation processes) in silica glasses as well as to distinguish ionization and displacement effects.

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