PILE IRRADIATION INDUCED 4.4-eV PHOTOLUMINESCENCE IN FUSED SILICA

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(Received 31 August 1997)

In pile irradiated type-I fused silica, strong photoluminescence (PL) was observed at \( \sim 4.4 \text{eV} \). The PL band was successfully decomposed into two Gaussian spectra due to the pile-induced \( B_2 \alpha \) band at 4.46eV and due to the intrinsic \( B_2 \beta \) band at 4.42eV, respectively. In addition, strong optical absorption (OA) was observed above \( \sim 4 \text{eV} \) in these samples. The OA band was also decomposed into six Gaussian OA bands at 6.5, 5.85, 5.53, 5.17, 5.06, and 4.86eV. Besides, the PL band at 1.9eV due to the NBOHC was observed. The above results indicated that pile irradiation induced the \( B_2 \alpha \) band by recoiling an oxygen atom, and the NBOHC and the \( E' \) center by the fission of the Si-O-Si bond.

Keywords: Fused silica glass; Radiation damage; Point defect; Photoluminescence; Optical absorption

I INTRODUCTION

Vitreous silica is more and more widely used in modern technologies. As one of its interesting applications, vitreous silica is one of the candidate window materials for laser nuclear fusion reactors. In this application, data about the effects of neutron irradiation on optical properties of vitreous silica are required.

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On the other hand, structures of diamagnetic point defects in vitreous silica have been studied mainly by means of optical methods such as optical absorption, photoluminescence and lifetime measurements for more than three decades [1]. Nevertheless, the structures of the diamagnetic point defects in vitreous silica have still been less clarified because of the restricted experimental methods.

One of the diamagnetic defects in vitreous silica is the $B_2$ band which was originally observed by Mitchell and Paige [2]. The $B_2$ band was distinguished into the $B_2\alpha$ band with an optical absorption (OA) band centered at 5.02 eV and a photoluminescence (PL) emission centered at 4.4 and 2.7 eV, and the $B_2\beta$ with an OA band at 5.17 eV and a PL emission at 4.2 eV [3,4].

It is well-known that the $B_2$ band is observed in oxygen deficient fused silica [5]. In terms of the structure of the $B_2\alpha$ band, the oxygen vacancy model [3,6] and the twofold coordinated Si model [7,8] have been proposed. However, the exact structure model is still open to question. The $B_2\alpha$ band is also observed in vitreous silicas irradiated by neutrons [9,10], by ions [11] by electrons [12] or by electromagnetic waves such as $\gamma$-rays [13-15], X-rays [16-18] or ultraviolet lights [16,19].

In this paper we are concerned with the effect of pile irradiation on the PL band at 4.4 eV in fused silica. We compared the pile induced PL band with the intrinsic $B_2\beta$ band, as observe in oxygen deficient fused silica. Finally we present the 1.9 eV PL which seems to be due to the NBOHC induced by pile irradiation.

II EXPERIMENTAL

Samples investigated were commercially available fused silica glasses, GE214 (type I OH content: ~ 5 wppm) with mirror polished surfaces whose dimensions were $10 \times 10 \times 1$ mm$^3$. These samples were irradiated for 50 h in the VT-8 of JRR2 where nominal fast neutron flux and nominal dose rate of gamma rays are $2.1 \times 10^{11}$ nvt and $1.0 \times 10^5$ Gy/h, respectively, and the ambient temperature was below 350 K. Then total fast neutrons fluences and gamma rays doses are $3.8 \times 10^{16}$ nvt and $5.0 \times 10^6$ Gy, respectively. We neglect the effect of thermal neutrons on defect formations, because there are no thermal neutron nuclear reactions with silica or oxygen.
All optical measurements were made at room temperature. The OA spectra in the visible and ultraviolet region (6.2-1.5 eV) were obtained with a Hitachi U-3000 double beam spectrophotometer. The continuous wave PL and PL excitation (PLE) spectra were obtained with a Hitachi F-3010 fluorescence spectrophotometer. For the measurement of 1.9 eV PL, a filter cutting down above 3.3 eV (below 376 nm) was used to reduce the effect of double wavelengths (~580 nm, ~2.2 eV) due to the intense 4.4 eV PL.

III RESULTS AND DISCUSSION

Figure 1 shows the continuous wave PL emission spectra, measured by exciting with the 5.1 eV light corresponding to OA maximum in the as-manufactured sample. In the as-manufactured sample, a strong PL band and a weak one were clearly observed at 3.2 and at 4.22 eV respectively. In the pile irradiated sample, the strong PL emission at 3.2 eV decreased, while the weak PL emission at ~4.2 eV increased.

![Figure 1: Continuous wave PL spectra at ~3.2 eV and at ~4.2 eV excited by 5.1 eV in the pile irradiated GE214.](image)
and shifted from 4.22 to 4.38 eV. The PLE spectra monitored at 4.3 eV also shifted from 5.06 to 4.96 eV as shown in Fig. 2. Similar shifts of the PL and the PLE have been observed in the γ-ray irradiated vitreous silica by Boscanio et al. [13].

The detailed PL spectra at ~4.3 eV are shown in Fig. 3(a) and (b). The PL spectrum after pile irradiation was successfully decomposed into two Gaussian components, that is, a band at 4.22 eV and a band at 4.46 eV which correspond to the intrinsic B₂ β band and the pile-irradiation induced B₂ α band respectively as shown in Fig. 3. This suggests that in addition to the intrinsic B₂ β band, the B₂ α band is induced by recoiling an oxygen atom from a Si–O–Si bond under pile irradiation, and the observed spectra are composed of the B₂ α and the B₂ β band. This is the first try to separate the PL band at ~4.4 eV into the B₂ α band and the B₂ β band.

Besides the above results, the 1.9 eV PL and the corresponding PLE were observed as shown in Fig. 4, using a filter cutting down above 3.3 eV. The maximum of the PLE is 4.82 eV. This suggests that

![Graph](image-url)  
**FIGURE 2** PLE spectra monitored at 4.3 eV in the as-received GE214 and in the pile irradiated GE214.
FIGURE 3  (a) PL bands at $\sim 4$ eV in as-received GE214 and (b) those separated into two Gaussian bands in pile irradiated GE214.
the origin of the 1.9 eV appears to be due to the NBOHC and not due to the $^1D$ to $^3P$ transition of recoiled oxygen atoms. In addition, the half width of the 1.9 eV PL is 0.13 eV, which is too broad even for atoms in solid state.

Figures 5 and 6 show the OA spectra in the as-manufactured sample (GE214) and in the pile-irradiated sample. In the as-manufactured sample a weak OA band around 5.1 eV, usually observed in oxygen deficient type silica having the $B_2 \beta$ band [1], is detected in the wavelength range of 6-2 eV. In the pile-irradiated sample, a weak OA shoulder around 5.1 eV due to both the intrinsic $B_2 \beta$ band and the probably pile-irradiation induced $B_2 \alpha$ band was observed in addition to a relatively intense OA band at 5.85 eV due to the $E'$ centers on the tail or more intense OA band above 6 eV. The OA spectrum was fitted by five Gaussian OA bands at 4.85 ± 0.4 (NBOHC), 5.06 ± 0.175 ($B_2 \alpha$), 5.17 ± 0.24 ($B_2 \beta$), 5.85 ± 0.31 ($E'$ center) and 6.5 ± 0.41 eV ($B_2 \alpha$) as shown in Fig. 6. Although the uniqueness of the Gaussian resolution of the overlapping optical
FIGURE 5  Optical absorption spectra in the as-received GE214.

FIGURE 6  Optical absorption spectra in the pile irradiated GE214 separated into six Gaussian bands.
bands is open to question, the fits of Fig. 6 plausibly demonstrate that such bands may be produced in the pile irradiated samples. From this figure, it is noticed that a band at $\sim 5.5\text{ eV}$ appeared after the fittings. The origin of this band is not identified, but similar bands at $5.4\text{ eV}$ are reported in the literatures [15,18].

We conclude tentatively that in fused silica, pile irradiation induced the B$_2$ $\alpha$ band by recoiling an oxygen atom, and the NBOHC and the E' center by the fission of the Si–O–Si bond. However, any recoiled oxygen atoms were not detected.

Acknowledgements

The authors acknowledge Mr. H. Murakami, the President of Soei Tsusho Company, Ltd. for his financial support.

References