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# Luminescence in $SiO_2$ induced by MeV energy proton irradiation

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**Abstract**

Ion-induced luminescence was measured at room temperature for $SiO_2$ glasses with different OH concentration during irradiation by protons with 0.2–2 MeV energies. In addition to a prominent peak at 460 nm, characteristic peaks were detected at 390 and 650 nm, depending on the OH contents. For silica glasses with lower OH, the 390 nm luminescence appeared at a low dose and its intensity decreased quickly with an increase of the ion dose. The higher intensity for the 650 nm luminescence, related with the non-bridging oxygen hole centers, was found for higher OH concentration. On the other hand, the luminescence at 460 nm was not efficiently emitted from the silica glasses with higher OH when irradiated by MeV protons with low-electronic energy loss.


## 1. Introduction

Understanding irradiation effects on silica based materials is very important from the standpoint of developing optical functional materials such as optical fibers and windows, which can be used for diagnostics in fusion devices [1]. It is well known that doping with impurity elements can improve radiation resistance for optical absorption. Recently, hydrogen-treatment has been successfully applied to silica-based optical fibers to improve the transmission properties during irradiation [2]. Although there are possible mechanisms for the reduced degradation by irradiation, the effects of oxyhydrate (OH) and hydrogen (H, $H_2$) on defect formation by the irradiation has not yet been clarified.

Among several experimental techniques, ion-beam induced luminescence (IBL) can be used to detect non-paramagnetic defects in $SiO_2$, by probing up to about 20 μm below the surface [3]. Luminescence measurements during ion bombardment are especially useful because they allow us to monitor the dynamic processes involved in damage creation, excitation and relaxation of the glass network. In comparison with the photoluminescence (PL) technique, the energetic ions provide high intensity electronic excitation along their trajectories, and a simple binary collision model can specify the nuclear and the electronic energy deposition rates in a certain depth. On the other hand, both the nuclear collisions and the electronic excitation can introduce defects responsible for creating light emission centers, which leads to some complexity in clarifying luminescence mechanisms. In the present paper, ion-beam-induced luminescence of silica glasses was investigated in connection with intrinsic OH during MeV proton irradiation.

## 2. Experiments

Specimens used in the present experiments were commercially available fused silica glasses (T-2030 and T-1030) and synthesized silica glasses (T-4040) produced by Toshiba Ceramics, Co. Ltd. The OH contents of each specimen are 1, 200 and 800 wt. ppm for T-2030, T-1030

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and T-4040, respectively. The specimens were cut into a size of 10 mm × 10 mm with a thickness of 0.5 mm. Measurements of ion-beam-induced luminescence were performed in a scattering chamber with a base pressure of $2\times10^{-6}$ Pa, connected to a 1.7 MV tandem accelerator at the Laboratory for Developmental Research of Advance Materials, Institute for Materials Research, Tohoku University. The specimen was irradiated by proton in the energy range 0.2–2 MeV up to a dose about $10^{16}$ ions/cm$^2$ at ambient temperature. An ion beam of about 1 mm diameter was incident on the specimen at an angle of 40° with a flux density of 0.1–1 μA/cm$^2$ corresponding to $0.6–6\times10^{12}$ ions/cm$^2$. During the ion irradiation, ion-induced luminescence was transmitted by an optical fiber inserted in the vacuum chamber, and was detected with a multi-channel spectrum analyzer (Hamamatsu C5967, 5098).

## 3. Results and discussions

Fig. 1 shows typical luminescence spectra of three types of silica specimens (T-2030, T-1030 and T-4040) with different OH concentration, measured under 1.5 MeV proton irradiation at doses of $4.0\times10^{13}$ and $1.3\times10^{15}$ H/cm$^2$. The luminescence intensities are normalized with the incident proton current. In the visible range, we found three peaks, at wavelength of 390, 460 and 650 nm from the specimens. For the fused silica specimen having the lowest OH concentration (T-2030), a prominent peak at 390 nm appeared at the very beginning of the irradiation, at doses below $10^{14}$ H/cm$^2$. No peak was observed around 460 and 650 nm. At higher irradiation dose, the peak intensity at 390 nm diminished and an intense peak at 460 nm was observed. Two peaks of 460 and 650 nm were observed from the beginning of the proton irradiation, but no intensity was found at 390 nm for the synthesized silica specimen with OH of 800 wt. ppm. The specimen T-1030 having an OH content of 200 wt. ppm showed luminescence spectra intermediate between those of T-2030 and T-4040. The luminescence at 650 nm is believed to be related to the non-bridging oxygen hole center (NBOHC) [4]. It is well known that the NBOHCs can be created by hydrogen displacement from the oxyhydrate during irradiation [5]. Thus, the observed intensities of the 650 nm peak in the three different specimens were qualitatively consistent with their nominal OH contents. Although blue luminescence centered at 460 nm was dominant at higher doses for all specimens, shoulders at around 390 nm were still observed for fused silica specimens with low-OH (T-1030 and T-2030).

Fig. 2 shows the dose dependence of the luminescence intensities for the three peaks during 1.5 MeV proton irradiation. Here we plot the observed intensity for each peak, normalized by the incident proton current density.

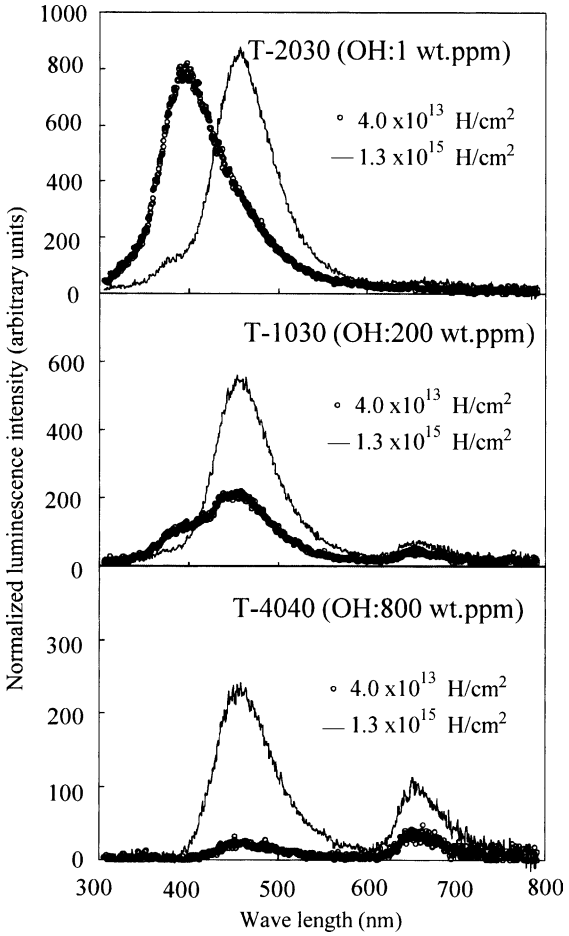


Fig. 1. Typical ion induced luminescence spectra for three types of silica with different OH concentrations (1, 200 and 800 wt. ppm OH), obtained under the 1.5 MeV proton irradiation at room temperature to doses of $4.0\times10^{13}$ and $1.3\times10^{15}$ H/cm$^2$.

In brief, the intensity of the 460 nm peak increased with increasing incident proton dose in each type of specimen, although the normalized intensities were quite different among the three specimens. Specimens with higher OH concentration emitted lower intensity of the 460 nm luminescence at the same proton dose. This suggests that the formation of defects responsible for the 460 nm luminescence is suppressed, and/or the excitation energy is dissipated without light emission in higher OH silica. The 460 nm peaks are considered to be related to oxygen-deficiency-centers (ODCs) assigned to the $B_{2\alpha}$ band corresponding to the excitation energy of 7.7 and 5.05 eV [6,7]. If NBOHCs are created in high-OH silica during irradiation, the displaced hydrogen can be trapped in ODCs, producing H(I) centers [8]. Therefore, the lower intensity of 460 nm luminescence might be attributed to the higher concentration of OH, which are able to transform ODCs to other type of defects, such as

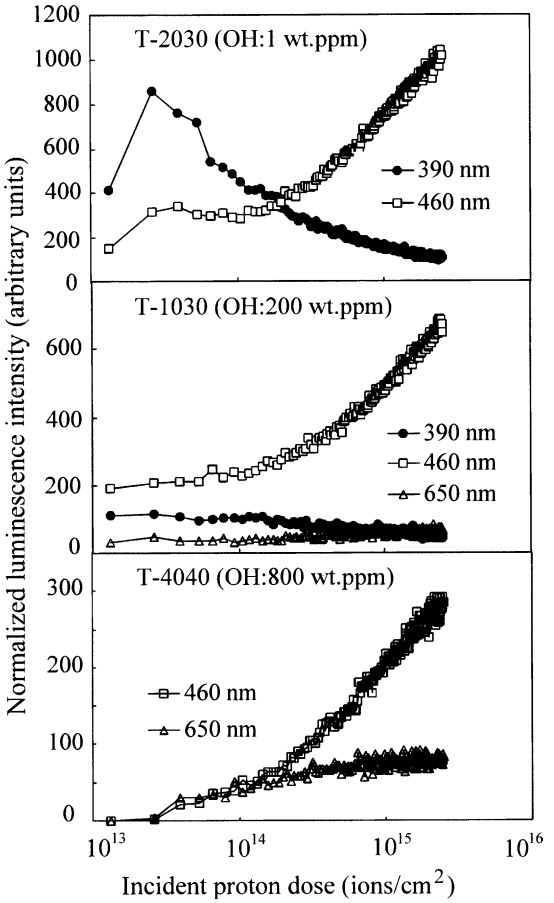


Fig. 2. Luminescence intensities of three types of silica with different OH concentration during 1.5 MeV proton irradiation at room temperature, plotted against incident proton doses.

H(I) centers. The luminescence at 650 nm was not observed for the specimen with lowest OH (T-2030). In specimens with higher OH, the 650 nm peak intensity increased at the beginning of the irradiation, and became constant at higher doses. This fact indicates that the population of NBOHCs did not change drastically during the subsequent proton irradiation. Though the 460 and 650 nm luminescence intensity increased with incident proton dose, the 390 nm peak quickly diminished even at a very small dose, especially for the specimen with the lowest OH (T-2030). The present results on 390 nm luminescence are consistent with radio luminescence measurements using a gamma-ray source and a fission reactor [9], in which the 390 nm peak was found for low-OH fused silica (T-2030) and decreased slowly under gamma ray and quickly under neutron irradiation. However, none of the earlier measurements of MeV ion induced luminescence mentioned the 390 nm peak [10,11]. The 390 nm luminescence is thought to be attributed to ODCs assigned to the $B_{2\beta}$ band corresponding an excitation energy of 5.1 eV [12]. It was proposed that the $B_{2\beta}$ band is transformed to an $E'$ center by gamma ray irradiation [13]. Because the density of electronic energy deposition along the incident ion trajectory is quite large in comparison with that by gamma rays, the 390 nm emission centers can be easily transformed to other types of defects by a small amount of ion penetration.

In Fig. 3, luminescence intensities by proton irradiation for each peak (390, 460 and 650 nm) are plotted against the nominal OH concentration (wt. ppm) of the specimens. The intensities for peaks at 460 and 650 nm were taken at the dose of $1.3\times10^{15}$ H/cm$^2$, and those for 390 nm were taken at the low dose of $4.0\times10^{13}$ H/cm$^2$. As described above regardingly the 650 nm peak, the larger intensity for higher concentration of the OH in the specimen is consistent with the relationship between NBOHC and OH concentration. Although the irradiation dose dependence of the intensity of the 390 and 460 nm peaks opposed each other, both intensities decreased with an increase of OH concentration. It is worthwhile to compare with previous results from lower energy ion induced luminescence experiments [14], in which the 460 nm emission intensity monotonically increased with OH content under 20 keV $D^+$ irradiation. Also, in a fission reactor reactor irradiation, a stronger 450 nm peak intensity was observed for higher OH silica (T-4040, T-1030), but was not detected for low-OH fused silica (T-2030) [9]. For keV energy ion irradiation or in the fission reactor, nuclear collisions play an important role for creating the ODCs corresponding to the blue luminescence at 460 nm The oxyhydrate may help to create more ODCs, and hydrogen trapping by ODCs may be

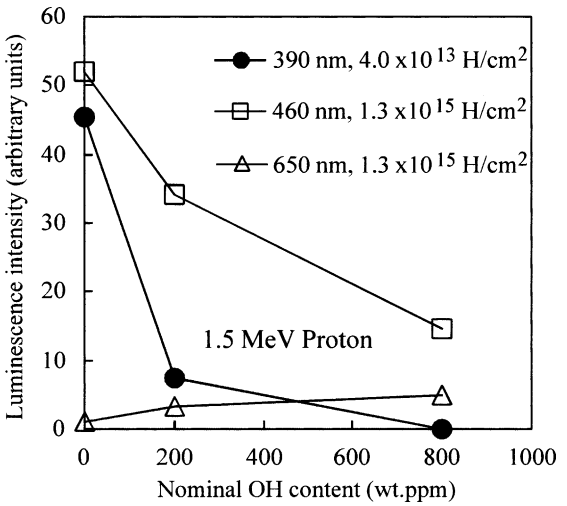


Fig. 3. Luminescence intensities of three peaks (390, 460 and 650 nm) obtained for 1.5 MeV proton irradiation, plotted against nominal OH concentration of the specimens.

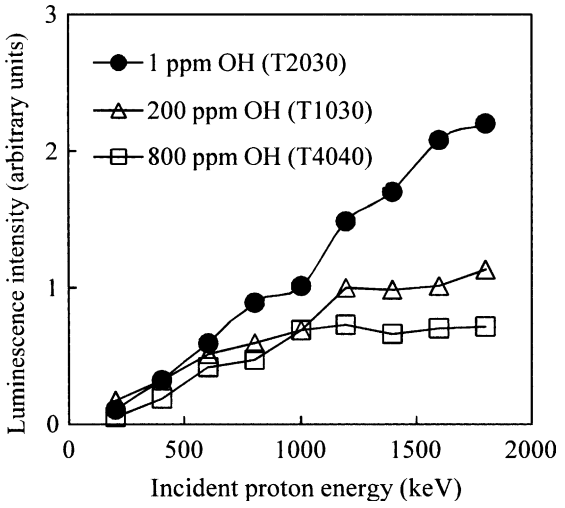


Fig. 4. Luminescence intensities for the 460 nm peaks are plotted against the incident proton energy for three silica specimens with different OH concentration.

suppressed due to collisional cascades. On the other hand, electronic energy loss is three orders of magnitude larger than the nuclear energy loss for the MeV proton. Thus, oxygen vacancies are supposed to be created by MeV proton's electronic excitation [15], which may not interrupt transformation of ODCs to other types of defects.

We examined the incident proton energy dependence of the 460 nm luminescence intensity at an incident proton dose of about $1\times10^{15}$ H/cm$^2$ as shown in Fig. 4. The intensity of the 460 nm peak from the silica with lowest OH concentration (T-2030) linearly increased with increasing incident proton energy in the range between 0.2 and 2.0 MeV. But, the proton energy dependence of the 460 nm luminescence for the higher-OH silica is different from that for the lowest-OH silica. The luminescence intensity from OH-containing specimens (T-1030 and T-4040) tended to saturate at higher energies, indicating that the higher energy protons scarcely emitted the blue luminescence in high-OH silica. At higher proton energies, lower electronic energy loss may contribute less to the creation of defects, and may less stimulated light emission at 460 nm in the silica with high-OH concentration. The difference of the intensity among the three specimens was small for lower incident energies which have higher stopping cross section. Further investigation is necessary to clarify the effects of OH on defect formation in connection with electronic and nuclear energy loss of the incident ions.

## 4. Summary

We have measured the ion-induced luminescence of silica glasses to investigate defect formation during MeV energy proton irradiation, and the effects of OH. The intensities of the luminescence at 390, 460 and 650 nm wavelengths apparently depended on the nominal OH concentration in the specimen. The intensity of the 650 nm peak varied with the OH concentration, consistently indicating that the luminescence originated in the non-bridging oxygen hole centers. The 390 nm luminescence was clearly observed at the beginning of the proton irradiation for the fused silica with low-OH concentration, and quickly diminished with an increase of the ion dose, probably owing to transformation to other defects types. An MeV energy proton with lower electronic stopping resulted in intense luminescence at 460 nm from low-OH silica. In high-OH silica, however, the reduced electronic excitation may not effectively create $B_{2\alpha}$ emission centers by trapping hydrogen, and/or electronic excitation can dissipate without light emission.

## References

[1] A. Morono, E.R. Hodgson, J. Nucl. Mater. 258–263 (1988) 1889.
[2] D.L. Griscom, J. Appl. Phys. 80 (1996) 2142.
[3] R.J. Brooks, D.E. Hole, P.D. Townsend, Nucl. Instrum. and Meth. B 190 (2002) 136.
[4] L. Skuja, J. Non-Cryst. Solids 179 (1994) 51.
[5] M. Guzzi, M. Martimi, M. Mattaini, F. Pio, G. Spinolo, Phys. Rev. B35 (1987) 9407.
[6] L. Skuja, J. Non-Cryst. Solids 239 (1998) 16.
[7] H. Imai, K. Arai, H. Imagawa, H. Hosono, Y. abe, Phys. Rev. B38 (1988) 12772.
[8] V.A. Radzig, V.N. Bagratashvili, S.I. Tsypina, P.V. Chernov, A.O. Rybaltovskii, J. Phys. Chem. 99 (1995) 6650.
[9] T. Yoshida, T. Ii, T. Tanabe, H. Yoshida, K. Yamaguchi, J. Nucl. Mater. 307–311 (2002) 1268.
[10] P.J. Chandler, F. Jaque, P.D. Townsend, Raddiat. Eff. 42 (1979) 45.
[11] K. Moritani, I. Takagi, H. Moriyama, J. Nucl. Mater. 312 (2003) 97.
[12] L.N. Skuja, A.N. Trukhin, A.E. Plaudis, Phys. Stat. Sol. (a) 84 (1984) 153.
[13] A.V. Amossov, A.O. Rybaltovsky, J. Non-Cryst. Solids 260 (1994) 75.
[14] M. Fujiwara, T. Tanabe, H. Miyamaru, K. Miyazaki, Nucl. Instrum. and Meth. B 116 (1996) 536.
[15] H. Hosono, H. Kawazoe, N. Matsunami, Phys. Rev. Lett. 80 (1988) 317.