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## **Formation of CO<sub>2</sub> gas and OH groups in CR-39 plastics due to gamma-ray and ions irradiation**

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### **Abstract**

FT-IR spectral studies have been made for CR-39 detectors irradiated by gamma-rays, protons and carbon ions. An absorption peak for CO<sub>2</sub> appeared and grew with the fluence. The peak height was found to decrease gradually by storing in air. Absorbance of the OH group produced by ion bombardment was observed separately from that of adsorbed water using a FT-IR system on the beam line. The concentration of OH group would govern the rate of penetration of chemical agents along the track.

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*Keywords:* Latent track; CR-39; FT-IR; CO<sub>2</sub>; OH group; Radiation damage

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## 1. Introduction

It has been confirmed that CO<sub>2</sub> is produced in CR-39 detectors irradiated by various kinds of ions or low-LET radiation (El-Shahawy et al., 1992; Chong et al., 1997; Saad et al., 2001; Malek et al., 1999, 2002). The ejection of CO<sub>2</sub> and CO gases from the bombarded CR-39 and the decrease of the density of C=O and C-O-C bonds in it have also been pointed out (Rickards et al., 1992; Gagnadre et al., 1993; Darraud et al., 1994; Gerstener et al., 1999). These facts suggest that the carbonate ester bonds in CR-39 are destroyed by the exposures. However, the resultant structure of the damage, in other words, what is left after the CO<sub>2</sub> release, is still not clear. As one of the possible end-points, the OH group has been observed (Yamauchi et al., 2000, 2001). It is difficult to discriminate the OH group absorption band from that of adsorbed water because of the hygroscopic property of CR-39 (Malek et al., 2000; Yamauchi et al., in press). In the present work, a series of FT-IR measurements has been made for the CR-39 plastics irradiated by gamma-rays, protons and carbon ions. The formation and the release of CO<sub>2</sub> gas have been observed. The production of OH group was confirmed using an improved FT-IR system on the beam line.

## 2. Materials and experiments

A Japanese CR-39 detector, BARYOTRAK (Fukuvi Chemical Industry Co., Ltd., Japan), was utilized throughout this work. Two types of BARYOTRAK were used with different thickness of 950  $\mu\text{m}$  and 100  $\mu\text{m}$ . A molecular structure and the main orbitals of the monomer are shown in Fig. 1. They were reconstructed using a semi-empirical quantum chemical program of Win-MOPAC 3.0 (Fujitsu Co., Ltd., Japan). A calculated IR spectrum using the program is shown in Fig. 2, in which the oscillating strength, that is proportional to the absorbance, is plotted against the wavelength. Except from a slight shift of the peak position, the spectrum is well reconstructed.

Gamma irradiation was performed in air using an intense Co-60 source in the Institute for Scientific and Industrial Research, Osaka University, Japan. The IR spectra were measured using a conventional device (Shimadzu Corp., model FTIR-8100). The

first measurements were made within 1 day after the exposure.

Ion irradiations were made in vacuum at a tandem Van de Graaff in Kobe University of Mercantile Marine with protons (3.4, 3.2, 2.4, 2.2, 1.34 and 0.66 MeV) and carbon ions (8.5 and 7.5 MeV). The total fluence ranged from  $10^{10}$  to  $10^{14}$  ions/cm<sup>2</sup>. The ATR method was applied to 950  $\mu$ m thick CR-39 for the full spectrum. A portable FT-IR spectrometer (Travel IR, Sens IR Technologies, USA) was set near the beam line, which enabled us to make the first measurement within 1 min after the air-leak. On the other hand, the conventional spectrometer was operated in the transmittance mode for the observation of CO<sub>2</sub> and OH groups for the 100  $\mu$ m thick samples. The first measurement was made within 2 min after the air-leak. Another portable IR spectrometer (SpindliR, S.T. Japan Inc., Japan) was optically connected via ZnSe vacuum windows, mirrors and a sample holder in the chamber, to the IR detector. Its unique interference mechanism made it possible to obtain the IR spectra in vacuum, despite vibration produced by vacuum pumps.

### 3. Results and discussion

Typical IR spectra of CR-39 are shown in Fig. 3, plotting the transmittance as a function of the wave number. The broken curve shows the spectrum measured before irradiation. The spectrum with solid curve was attained after being exposed to 3.4 MeV protons at a fluence of  $4.0 \times 10^{13}$  ions/cm<sup>2</sup> and then stored in air for 60 min. The absorption at peaks corresponding to the C=O bond (1745 cm<sup>-1</sup>) and C-O-C bond (1140 and 1100 cm<sup>-1</sup>) decreased (Gagnadre et al., 1993). On the other hand, a sharp absorption peak of CO<sub>2</sub> (2340 cm<sup>-1</sup>) appeared. These spectral changes indicate that the carbonate ester bonds in the CR-39 chain would be broken by the irradiation. Another absorption peak around 3500 cm<sup>-1</sup> was assigned to OH group and/or adsorbed water (Gagnadre et al., 1993; Malek et al., 2000).

Transmittance at the main peaks depends on the fluence of 8.5 MeV carbon ions as shown in Fig. 4. Each IR observation started 1 min after the air-leak. The absorption at peaks for C=O and C-O-C decreases with the fluence, while the absorbance for CH<sub>2</sub> slightly increases with the fluence. In the previous Raman study,

the intensity of CH<sub>2</sub> slightly decreased (Yamauchi et al., 2001). It should be a reflection of the complementary relation between IR and Raman spectra. The absorption for OH group increases monotonously with the fluence, while the absorbance for CO<sub>2</sub> reaches its maximum at 10<sup>13</sup> ions/cm<sup>2</sup> and then decreases.

The IR measurements for CR-39 samples of 100 μm thick with transmittance mode were attained 2 min after each air-leak. In Fig. 5, the IR spectra around the absorption band of CO<sub>2</sub> in the CR-39 irradiated by 3.2 MeV proton at indicated fluences are shown. Up to 5x10<sup>12</sup> ions/cm<sup>2</sup>, the absorbance at 2340 cm<sup>-1</sup> increases with the fluence. Above this fluence, the other absorption peak at 2370 cm<sup>-1</sup> becomes significant. As shown in this figure, CO<sub>2</sub> is generated almost proportionally to the fluence at least in the low fluence range. We noticed that the absorbance is weakened by storing the samples in air before the IR measurements. Malek et al. have reported the CO<sub>2</sub> diffusion in 500 μm thick CR-39 irradiated with X-ray and gamma-rays (Malek et al., 1999). The absorbance saturation behavior at higher fluences shown in Fig. 4 would be explained by the escape of CO<sub>2</sub> along the ion path.

In Fig. 6, IR spectra around the CO<sub>2</sub> band at 2340 cm<sup>-1</sup> corresponding to CR-39 irradiated by 1.34 MeV protons with a fluence of 6x10<sup>12</sup> ions/cm<sup>2</sup> are shown. The transmittance at CO<sub>2</sub> band increases with the storage time as shown in this figure. It was impossible to detect the CO<sub>2</sub> band at storage times longer than 1140 min. This implies that the generated CO<sub>2</sub> gas escaped from the sample during post-irradiation storage.

In Fig. 7, the absorbance of the CO<sub>2</sub> band at 2340 cm<sup>-1</sup> for CR-39 samples irradiated by ions with several qualities are shown as a function of the storage time before the measurements. The four series of data show the decreasing behavior of CO<sub>2</sub> absorbance with the storage time, and among the three curves corresponding to proton, the one corresponding to higher proton energy has larger values of absorbance above 10 min than the others. The decreasing curves corresponding to incident energies of 0.66, 1.34 and 2.4 MeV reach the zero level at storage times of about 300, 700 and 2000 min, respectively. This can be explained by the difference in the proton ranges, since the CO<sub>2</sub> positioned originally at a deeper layer needs a longer time to escape into air.

The time required for CO<sub>2</sub> escape is about 100 min in the case of 7.5 MeV

carbon ions, which is shorter than that measured for 0.66 MeV protons, in spite of having comparable ranges. This implies that the tracks of carbon ions have a larger diffusion coefficient of CO<sub>2</sub> than protons. The escaped CO<sub>2</sub> was expected to leave a cylindrical region with lower density along the ion path. As shown in Figs. 3 and 4, there is other absorption band assigned to the created OH or to adsorbed water. The sites left by escaped CO<sub>2</sub> gas might have been decorated by OH groups.

In Fig. 8, IR spectra in the region around the OH absorption band are shown both for unirradiated CR-39 and for gamma-irradiated CR-39. There are three peaks at 3470, 3550 and 3635 cm<sup>-1</sup>, which are assigned to be the first overtone of C=O band, OH band and/or the symmetric vibration of water, and the anti-symmetric vibration of water, respectively (Gagnadre et al., 1993; Malek et al., 2000). The absorption at the first two peaks increases with the absorbed dose, as well as the broad absorption at lower wavenumber, while the increase of the third peak is not significant. Because the concentration of C=O decreases with the fluence when the material is exposed to carbon ions (see Fig. 4), the observed increase in the absorption is not attributed to changes in the C=O density. There is a possibility that the adsorption of water enhances the absorption at the wavelength of interest, but its contribution is not dominant, because the changes in transmittance at the second and the third peaks are different from each other.

Variations of the IR spectra of the proton irradiated CR-39 with the time after the air-leak are shown in Fig. 9. The absorption increases with the storage time in air and the saturated spectra are attained within 60 min. This time is the same as that observed for well de-gassed un-irradiated CR-39 (Yamauchi et al., in press). After the measurements, the sample was evacuated and the equivalent IR observation was made again. We have obtained almost the same spectra as that presented in Fig. 9. Water adsorption contributes to the considered band to a certain extent. The created OH groups may be active-sites to retain the water.

It has not been possible to discriminate the absorption of OH group from that of water in IR measurements using the conventional spectrometer. We tried to make a discriminative measurement, by set-up of the FT-IR system on the beam line of the

accelerator. A preliminary result is shown in Fig. 10 for the proton irradiated CR-39 as well as the non irradiated one. It was found that the absorption of OH group (2nd peak) increased slightly by the irradiation, although the third peak is difficult to detect both before and after the irradiation.

#### **4. Closing remarks**

The CO<sub>2</sub> was formed resultantly by the break of the main chain of CR-39. The release of CO<sub>2</sub> gas would leave the damaged region with a lower density along the ion path. The observed OH group, that could serve as a water-attracting group, was also inferred to exist along the region. The concentration of OH group would govern the rate of penetration of chemical agents along the track.

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## Figure Captions

Fig. 1. Molecular structure model for the monomer of CR-39.

Fig. 2. Calculated IR spectrum of CR-39 using Win-MOPAC 3.0 program.

Fig. 3. IR spectra of CR-39 before and after irradiation of 3.4 MeV proton attained by ATR mode. The spectrum of irradiated CR-39 was attained at 1 h after the air-leak.

Fig. 4. Changes in transmittance at main absorption bands in CR-39 with the fluence induced by the irradiation of 8.5 MeV carbon ions. Every measurement was made at ATR mode, 5 min after the air-leak.

Fig. 5. IR spectra of CO<sub>2</sub> generated in proton irradiated CR-39 at the indicated fluences.

Fig. 6. Decrease of CO<sub>2</sub> concentration in irradiated CR-39 during storage in the air: 1.34 MeV proton,  $6.0 \times 10^{12}$  ions/cm<sup>2</sup>.

Fig. 7. Changes in transmittance at the bands for CO<sub>2</sub> with the time after air-leak.

Fig. 8. IR spectra of gamma-irradiated CR-39 around the band of OH group at various absorbed doses.

Fig. 9. IR spectra of proton irradiated CR-39 around the band of OH group at the indicated time after the air-leak.

Fig. 10. Generation of OH group in proton irradiated CR-39 before the air-leak.

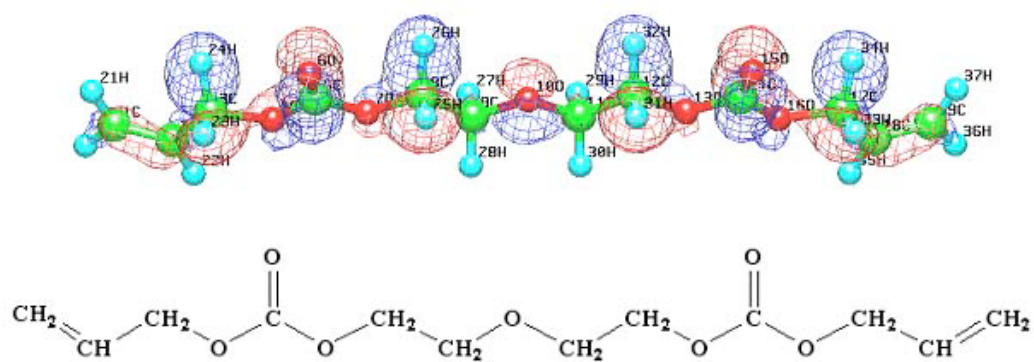


Fig. 1. T. Yamauchi et al.

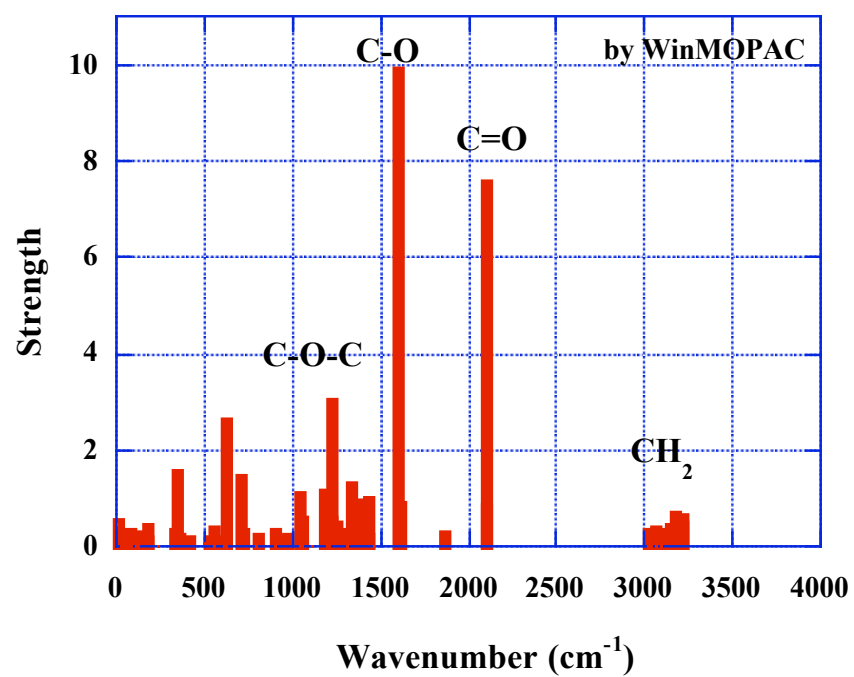


Fig. 2. T. Yamauchi et al.

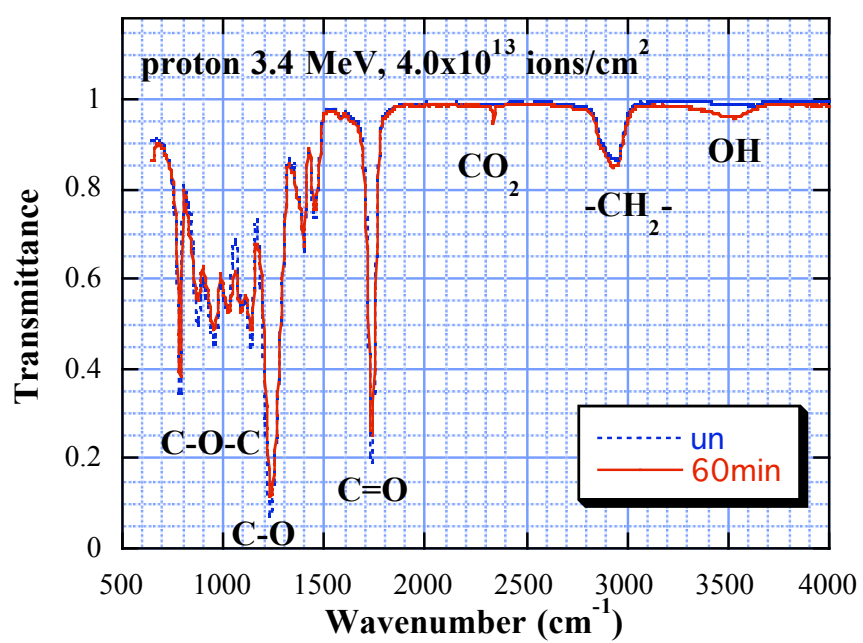


Fig. 3. T. Yamauchi et al.

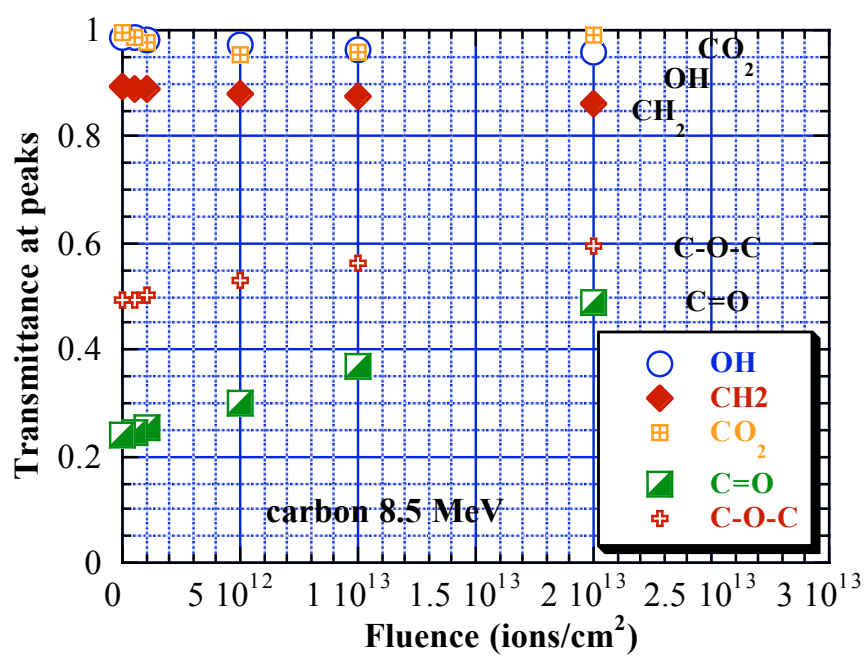


Fig. 4. T. Yamauchi et al.

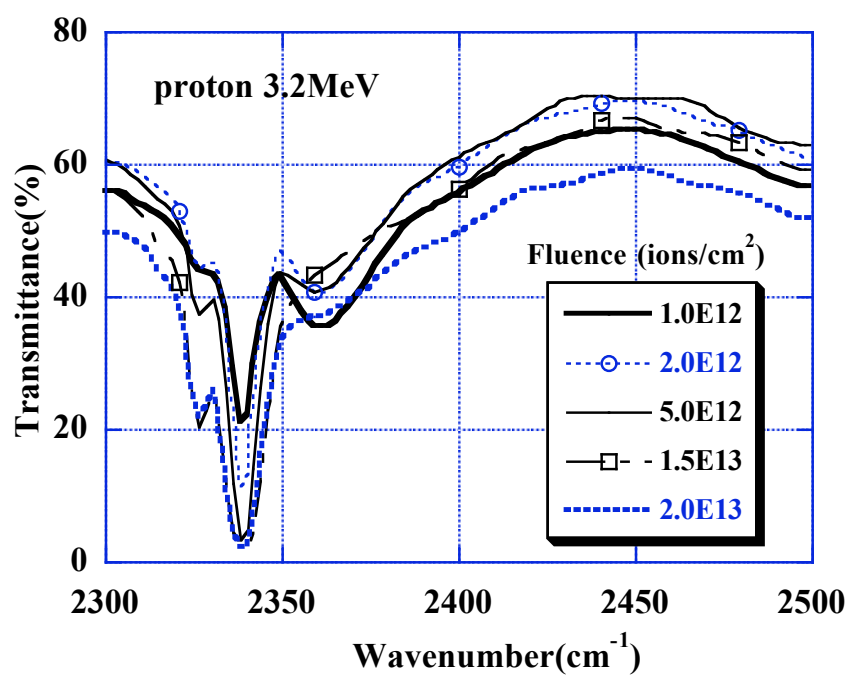


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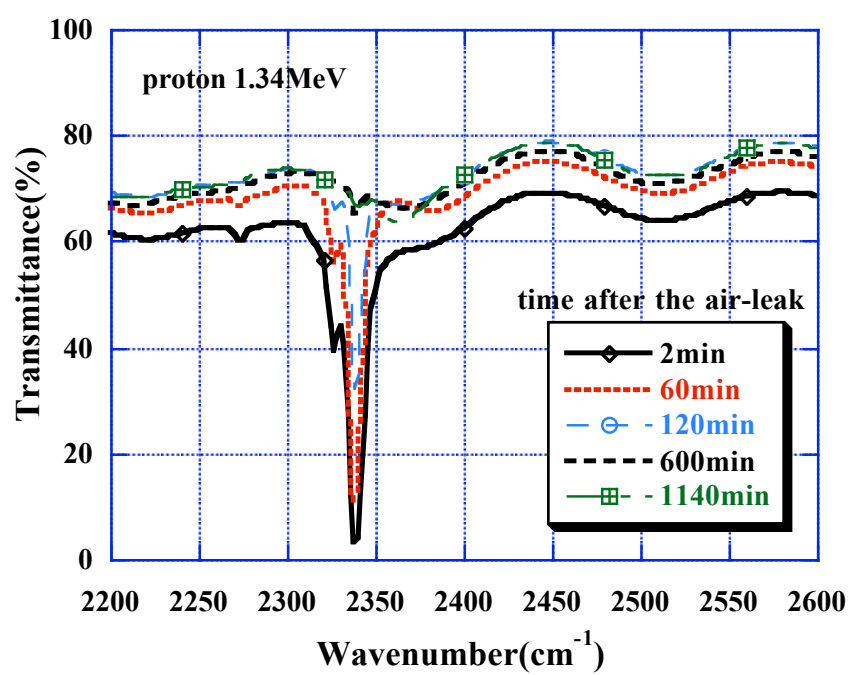


Fig. 6. T. Yamauchi et al.

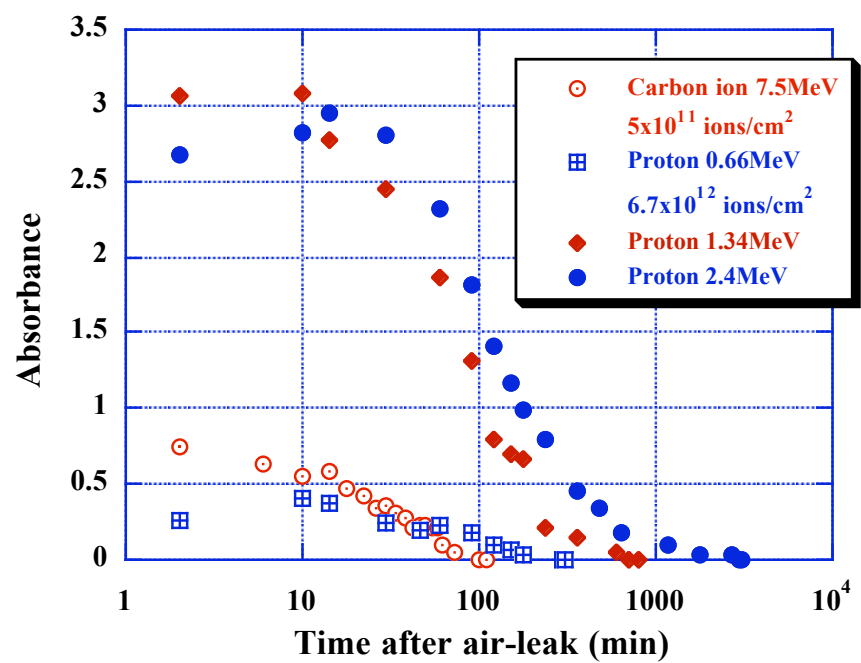


Fig. 7. T. Yamauchi et al.



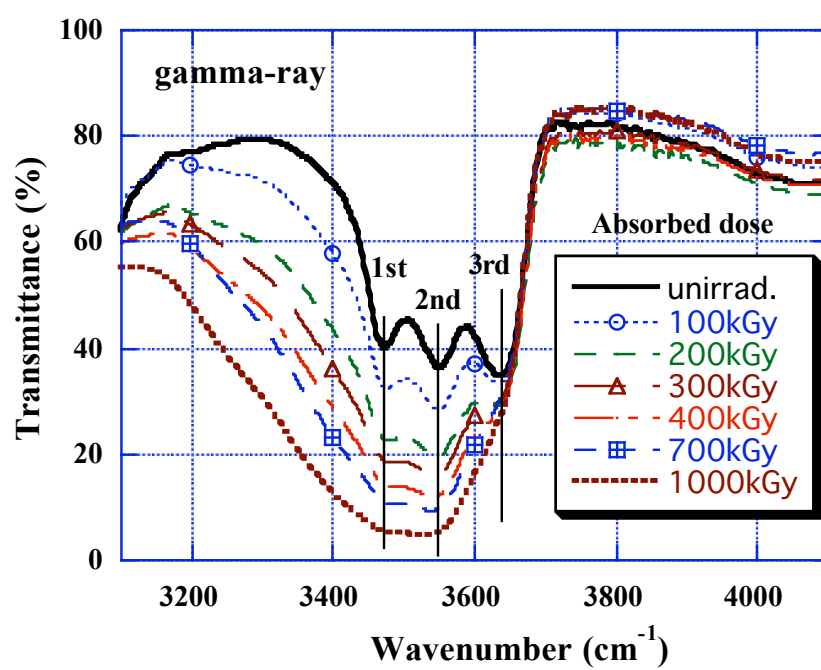


Fig. 8. T. Yamauchi et al.

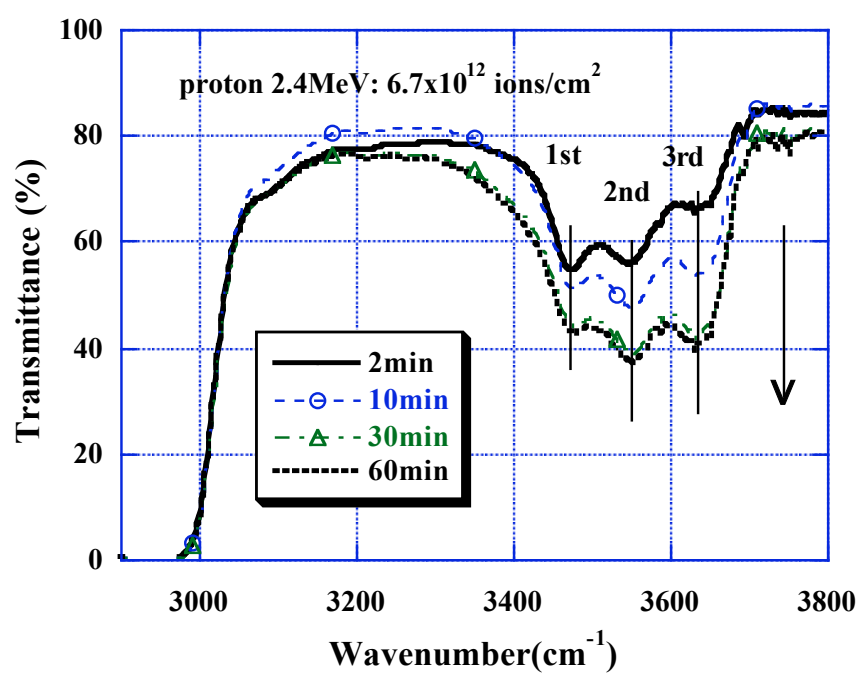


Fig. 9. T. Yamauchi et al.

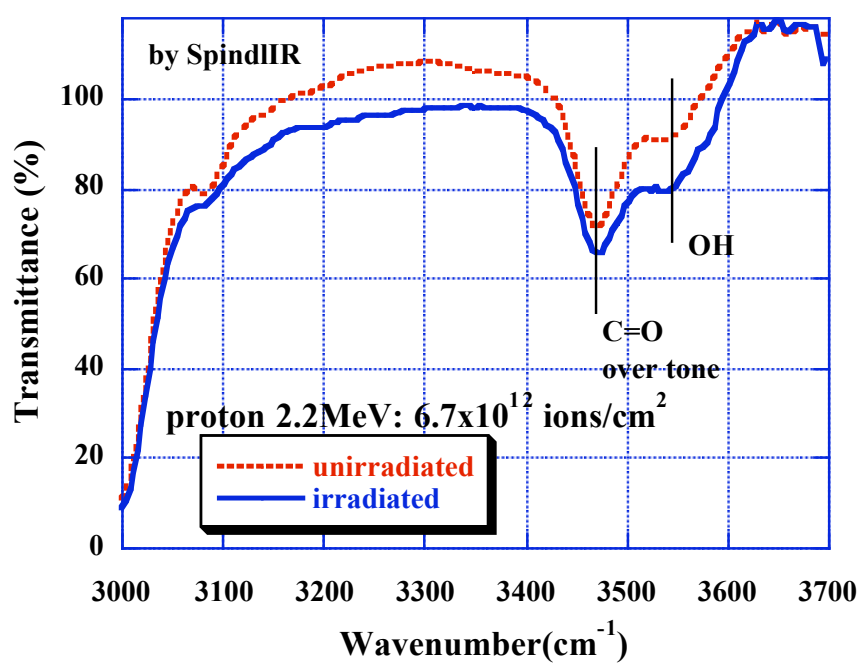


Fig. 10. T. Yamauchi et al.