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FT-IR study on interaction of irradiated deuteron with defects in Li_2O

Hisashi Tanigawa [a,*], Satoru Tanaka [b,1], Mikio Enoeda [a,2], Masato Akiba [a,3]

[a] *Japan Atomic Energy Research Institute, 801-1 Mukoyama, Naka-machi, Naka-gun, Ibaraki-ken 311-0193, Japan*
[b] *The University of Tokyo, 7-3-1 Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Abstract

The existing state of hydrogen isotopes in lithium oxide was studied using the Fourier transform infrared absorption spectroscopy. Infrared spectra in Li_2O single crystals irradiated by 1 MeV deuteron were recorded. Multiple peaks were observed in the O–D stretching vibration region under or after the irradiation. These peaks were attributed to the stretching vibrations of O–D present as $Li_2O–D^+$ in bulk Li_2O with defects. When the irradiated sample was annealed, a large peak attributed to the LiOD phase was observed. The present study shows that most of the implanted deuteron exists without O–D bonding in the bulk Li_2O crystal.

1. Introduction

It is necessary to evaluate tritium inventory for design of a breeding blanket and a fuel cycle in a fusion power plant. In the case of the breeding blanket with a solid breeder, defects will be introduced in ceramic breeding materials by a high dose irradiation of neutron. There is concern that these defects will increase the tritium inventory. Trapping of tritium by the defects is the reason; however, little is known about the detailed trapping process. The authors have been conducting both experimental and theoretical studies on behaviour of hydrogen isotopes in lithium oxide, emphasizing the interaction between hydrogen isotopes and defects. One method is an infrared absorption spectroscopy and another is a quantum chemical calculation [1–3]. Single crystals of Li_2O were studied because its simple structure makes easy to evaluate the interaction of hydrogen isotopes with the defects. In a series of studies, it was found that thermally doped defects, such as F-centers, could affect hydrogen isotopes in the bulk Li_2O and that hydrogen isotopes had several existing states due to the effects of the defects.

In the present paper, effects of irradiation defects are investigated. It is known that most of the hydrogen isotopes exist as H^+ forming O–H in Li_2O crystal [4]. Infrared absorption spectroscopy provides direct information about existing states of O–H. However, it is difficult to apply the method to irradiated crystals because the irradiated region is much smaller than the whole bulk crystal. In addition, a large amount of precipitates, such as Li_2CO_3 or LiOH, are produced on the surface of the irradiated samples and mask the signal from the bulk O–H when the samples are exposed to the air. Hence, O–D stretching vibrations in Li_2O crystal located in a vacuum chamber were observed under deuteron irradiation.

2. Experimental

Single crystals of Li_2O prepared by the floating zone growth method were used for investigations. The samples were disks about 8 mm in diameter and about 1 mm

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[*] Corresponding author. Tel.: +81-29 270 7514; fax: +81-29 270 7489.
E-mail address: tanigawh@fusion.naka.jaeri.go.jp (H. Tanigawa).
[1] Tel.: +81-3 5841 6969; fax: +81-3 5841 8625.
[2] Tel.: +81-29 270 7588; fax: +81-29 270 7489.
[3] Tel.: +81-29 270 7581; fax: +81-29 270 7489.

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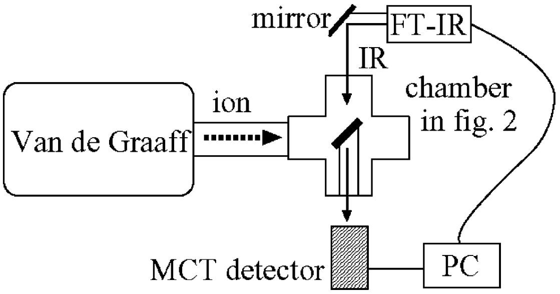

Fig. 1. Configuration of measurement system under irradiation.

thick. The specimens were irradiated with deuteron using a Van de Graaff accelerator at High Fluence Irradiation Facility (HIT), Research Center for Nuclear Science and Technology, the University of Tokyo. The specimen was located in the cross chamber that was connected to the beam line of the accelerator as shown in Fig. 1. Infrared absorption spectra were recorded using SHIMADZU, FT-IR8200PC. The infrared source was located above the chamber and the MCT detector cooled by liquid nitrogen below. The samples were positioned so that both ion beam and infrared light were injected at a 45° angle to the surface. The beam current was checked by inserting a Faraday cup in front of the sample.

Fig. 2 shows the configuration of the cross chamber. The chamber has two spectroscopic grade KBr windows sealed with rubber disks. The pressure of the chamber was kept at 10^{-4} Pa. The thermocouple was attached on the surface of the samples using a carbon tape. The stainless tube in which the samples were located was heated by a sheath heater. One mega-electronvolt deuteron was irradiated for 3 h with about 5 μA and fluence reached 3.5×10^{17} cm^{-2}. Under the irradiation, absorption spectra were recorded at a resolution of 2 cm^{-1} and the number of scans was 500. In this condition, it took 12 min for one measurement.

3. Results

3.1. Infrared absorption spectra of irradiated sample

Fig. 3 shows the infrared absorption spectra of Li_2O under and after the irradiation. The obtained spectra were divided by those from the non-irradiated sample and shown as transmittance. The temperature of the sample ranged from 473 to 573 K. This temperature rise was caused only by the irradiation and the sample was not heated by the heater. Under irradiation, a peak was observed at about 2515 cm^{-1}. After the beam stopped, this peak disappeared and a small peak at about 2603 cm^{-1} appeared. When the irradiation restarted, the peak at 2603 cm^{-1} was not observed and the peak at 2515 cm^{-1} was observed again. During the irradiation, the beam was shut off several times in order to check the current. The behaviour of the two peaks, at 2515 and 2603 cm^{-1}, was repeatable with the beam on and off. After the irradiation was finished, spectra were recorded consecutively. From the comparison of the first mea-

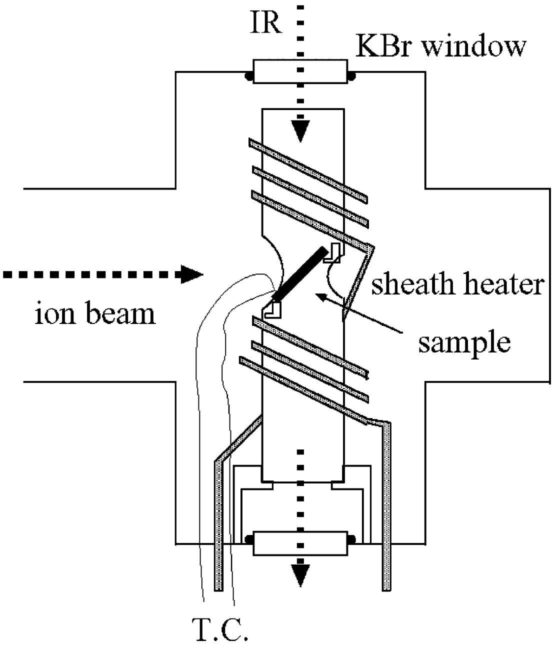

Fig. 2. Arrangement of sample in cross chamber.

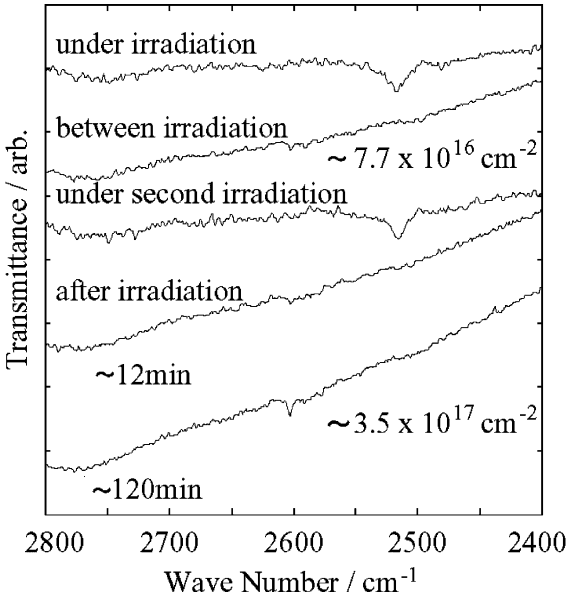

Fig. 3. Infrared absorption spectra of irradiated Li_2O crystal.

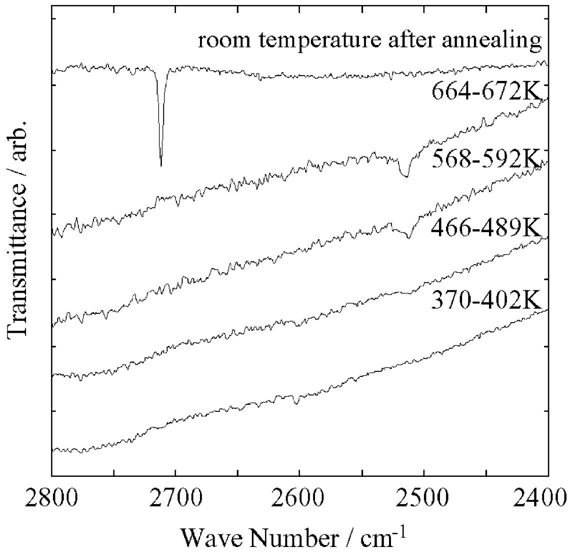

Fig. 4. Infrared absorption spectra of Li_2O crystal annealed after irradiation.

surement and 10th one, an increase in the intensity of the peak at 2603 cm^{-1} was found.

3.2. Infrared absorption spectra of sample annealed after irradiation

After irradiation, the sample was annealed in the chamber at the temperature up to 672 K and the absorption spectra were recorded. During each measurement, the temperatures of the sample were rising and not constant. Fig. 4 shows the observed absorption spectra during and after the annealing. The intensity of the peak at 2603 cm^{-1} decreased with annealing and the peak was not observed above 473 K. At higher temperatures than 473 K, a peak was observed at about 2512 cm^{-1}. This peak shifted to the higher wave number with increasing temperature. After the annealing procedure, a large peak at 2715 cm^{-1} was observed at room temperature. The intensity of the peak at 2715 cm^{-1} was much larger than other peaks that were observed under or after the irradiation.

4. Discussion

In the previous work, multiple peaks were observed in Li_2O single crystals that were treated by thermal absorption of D_2 and consequent quenching [1]. In the D_2 absorbed sample, the peak at 2510 cm^{-1} was observed above 473 K, which was attributed to O–D existing as a separate D^+ bonded with oxygen ions in the Li_2O crystal. This state has been expressed as $Li_2O–D^+$ in our papers [1,3]. The peak from $Li_2O–D^+$ shifted to higher wave number with increasing temperature. This behavior is very similar to that of the peak at 2512 cm^{-1} that was observed in the sample annealed after the irradiation. In the annealed samples, deuteron tends to exist in the most stable form at the thermal equilibrium in both the case of D_2 absorption and of D^+ irradiation. Therefore, the two peaks are attributed to the same O–D, existing in Li_2 $O–D^+$. In the D_2 absorbed sample, the peak from Li_2 $O–D^+$ was observed at 2515 cm^{-1} when the sample was annealed at 623 K. Under the irradiation, the temperature of the sample ranged from 473 to 573 K, however, the irradiated area could be locally much hotter than the monitored area. Therefore, the peak at 2515 cm^{-1}, observed under the irradiation, is attributed to O–D in $Li_2O–D^+$ form. In the irradiated crystal, defects of both lithium and oxygen are produced. From our quantum chemical calculation, it was shown that O–D neighboring a lithium vacancy was more stable than O–D with other kinds of defects [2]. In the annealed Li_2O crystal, Frenkel defects of lithium are dominant [5]. Therefore, it is suggested that the O–D in $Li_2O–D^+$ discussed here exists neighboring a lithium vacancy.

In the previous work, the peak of O–D affected by F-centers was observed at 2607 cm^{-1} for the quenched sample. The position of the peak observed after the irradiation, 2603 cm^{-1}, is close to that of the peak, 2607 cm^{-1}. In addition, both peaks disappeared when the samples were annealed. This behaviour is believed to be related to the recovery of F-centers. The mobility of lithium is much larger than that of oxygen in Li_2O crystals [6]. The defect of lithium can more easily recover than F-centers. Therefore, the density of F-centers is higher than that of lithium defects after the irradiation or the quenching treatment. Under irradiation, there existed a high density of lithium vacancies around the irradiated deuteron and the peak of 2515 cm^{-1} was observed. When the beam stopped, most of the lithium vacancies recovered and some F-centers still remained. These facts suggest that the peak of 2603 cm^{-1} observed after the irradiation is assigned to O–D affected by F-centers. As described above, the stability of O–D with a lithium vacancy is higher than that with F-centers. Hence, the peak of 2603 cm^{-1} decreased and the peak of 2515 cm^{-1} appeared again when the irradiation restarted.

The large peak, which was observed at 2715 cm^{-1} after the annealing, was attributed to O–D in the LiOD phase as identified in previous reports [1,7]. This means that the irradiated deuteron moved and aggregated into the LiOD phase during the annealing procedure. The intensity of the peak from LiOD was much higher than other peaks observed under or after the irradiation. This shows that most of the irradiated deuteron existed without O–D bonding. The trapping of deuterons by the irradiation defects would be the reason. For example, it was reported that F^0 center, oxygen vacancy trapping two electrons, could strongly trap a proton in Li_2O crystal from the quantum chemical analysis [2]. The increase of the peak at 2603 cm^{-1} observed after the irradiation suggests that some deuterons move from the trapping sites and form O–D bonds.

The present results indicate that hydrogen isotopes exist without O–H bonding in the highly defected Li_2O crystal although they are forming O–H bonding at thermal equilibrium. It has been considered that the major diffusion path of tritium in Li_2O is jumping between oxygen sites keeping O–T bonding [4]. The present study confirms the importance of the irradiation effects and suggests that there exists a different path of diffusion where tritium does not keep O–T bonding.

5. Conclusions

The stretching vibrations of O–D in Li_2O single crystal were recorded under the deuteron irradiation. The results are summarised as follows.

1. Most of the implanted deuterons existed without O–D bonding. By annealing after the irradiation, the intensity of the peak from O–D increased. This suggests that deuterons moved from the trapping center and formed O–D bonds.
2. Some of the implanted deuterons formed O–D and their peaks were observed at 2603 and 2515 cm^{-1}. The former was attributed to O–D affected by F-centers and the latter to O–D neighboring a lithium vacancy.

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