

Hydrogen isotope behavior in Li_2O at low temperature by FT-IR

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Abstract

The hydrogen isotope behavior in Li_2O at low temperature was studied by Fourier transform infrared spectroscopy (FT-IR) to clarify the fundamental behavior of hydrogen isotopes. In the IR spectra obtained under the deuterium ion irradiation at 228 K, three peaks at 2710, 2660 and 2605 cm^{-1} , and a broad peak at a region of 2700–2500 cm^{-1} were observed, corresponding to the O–D stretching vibrations. The O–D bonds as the broad peak changed to the LiOD phase as the temperature increased. In comparison with the results of irradiation at room temperature, (i) the formation of LiOD phase was restrained, and (ii) the broad peak could be apparently observed only in the low temperature irradiation. Therefore, it was concluded that the chemical states of hydrogen isotopes in Li_2O have a dependence on the sample temperature of the deuterium ion irradiation.

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1. Introduction

Lithium oxide (Li_2O) has been proposed as the blanket breeding material for the thermonuclear fusion reactor [1,2]. Predicting the recovery behavior of the hydrogen isotopes, especially tritium, from Li_2O , is one of the most critical issues for the assessment of fusion reactor safety. Many studies have been devoted to this subject in the last decade, and the important role of radiation defects, especially F centers, in determining the hydrogen isotopes behaviors has been pointed out [3]. However, the interaction of the hydrogen isotopes with radiation defects is not clearly understood.

In a previous study, the results of IR absorption analyses under the 3-keV deuterium ion (D_2^+) irradiation at room temperature (RT) were reported [4]. The chemical states of various O–D bonds in Li_2O were observed by Fourier transform infrared spectroscopy

(FT-IR), and the behavior of the irradiated hydrogen isotopes has been discussed with a focus on the influence of radiation defects. It was concluded that radiation defects increase the retention of hydrogen isotopes in Li_2O through enhancement of LiOD phase formation and increase of the amount of the O–D bonds affected by defects [4].

In the present study, the sample temperature was controlled at low temperature by an in situ temperature controlled FT-IR system. Deuterium ions irradiated a Li_2O sample at the low temperature, and the fundamental behavior in the Li_2O including the formation of the LiOD phase was studied.

2. Experimental

The Li_2O single crystal grown by the floating zone method [5] was cut into a disk with a diameter of 8 mm and a thickness of 1 mm to be used as a sample. The sample was annealed in a furnace under 1×10^{-4} Pa vacuum at 973 K for one day in order to decompose the impurities formed on the sample, such as LiOH and

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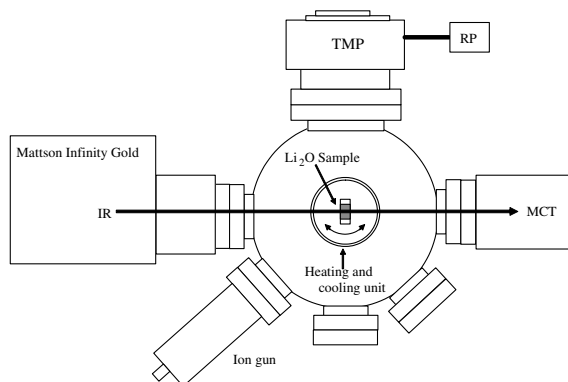


Fig. 1. Schematic view of the in situ temperature controlled FT-IR system.

Li_2CO_3 . Subsequently, the sample was loaded into the in situ temperature controlled FT-IR system and was annealed again in a vacuum below 10^{-6} Pa at 923 K until the IR absorption peaks related to LiOH and Li_2CO_3 disappeared completely.

A schematic drawing of the in situ temperature controlled FT-IR system is shown in Fig. 1. The Li_2O sample was located in the center of the vacuum chamber. Liquid nitrogen was introduced into the heating and cooling unit, and the sample holder was cooled down through copper wires connected with the unit. The sample was cooled below 193 K, and the sample temperature was kept constant by controlling the heating unit.

After stabilizing the temperature at 213 and 300 K, the Li_2O sample was irradiated with deuterium ions with an energy of 3 keV, flux of $1.3 \times 10^{17} \text{ D m}^{-2} \text{ s}^{-1}$ and fluence up to $1.0 \times 10^{22} \text{ D m}^{-2}$. During the deuterium ion irradiation, the sample temperature increased to 228 and 323 K. The FT-IR spectra were achieved by using a Mattson Infinity Gold system continuously during and after the deuterium ion irradiation. After the deuterium ion irradiation, the sample irradiated at 228 K was heated isochronally to 283 K, and the hydrogen behavior in Li_2O was also studied.

3. Results and discussion

Fig. 2 shows the FT-IR spectra of the Li_2O samples after the deuterium ion irradiation at 323 and 228 K. A large peak was observed at the wave number of 2710 cm^{-1} , namely a O–D bond existing as a LiOD phase [4,6]. Two small peaks were also found in both experiments at the wave numbers of 2660 cm^{-1} (a surface O–D bond with several adjacent O–D bonds [4,7]) and 2605 cm^{-1} (an O–D bond affected by defects in the bulk [4,8]). However, a broad peak was observed in the range

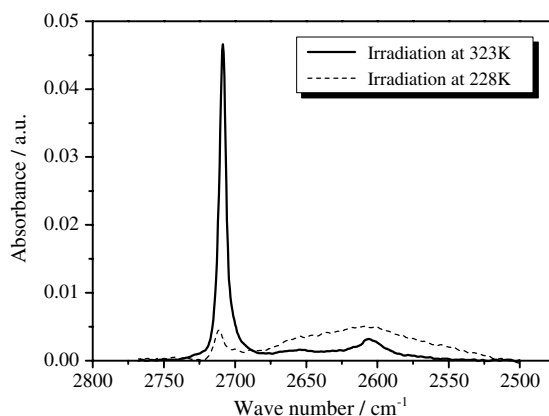


Fig. 2. FT-IR spectra of Li_2O after deuterium ion irradiation ($1.0 \times 10^{22} \text{ D m}^{-2}$) at 323 and 228 K.

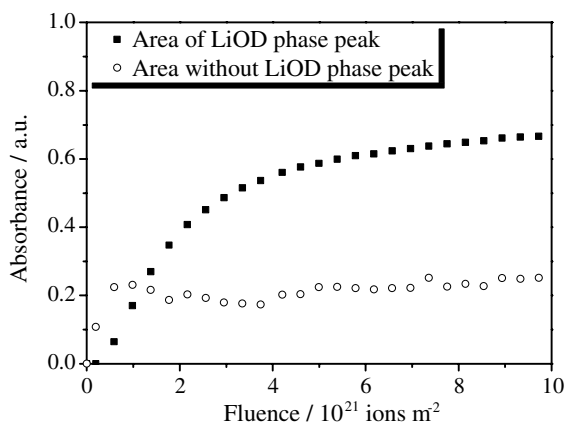


Fig. 3. Dependence of the areas of LiOD phase peak and the other peaks at 323 K on the deuterium ion fluence.

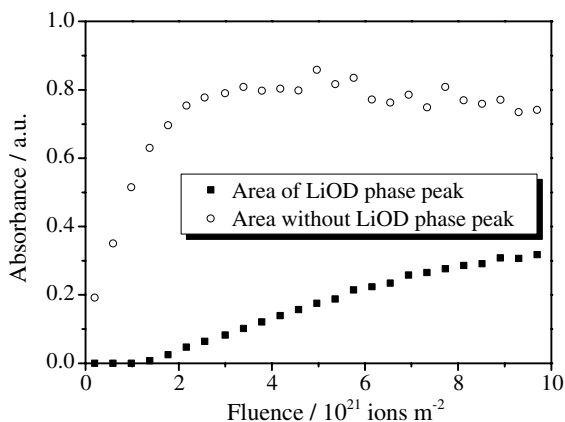


Fig. 4. Dependence of the areas of LiOD phase peak and the other peaks at 228 K on the deuterium ion fluence.

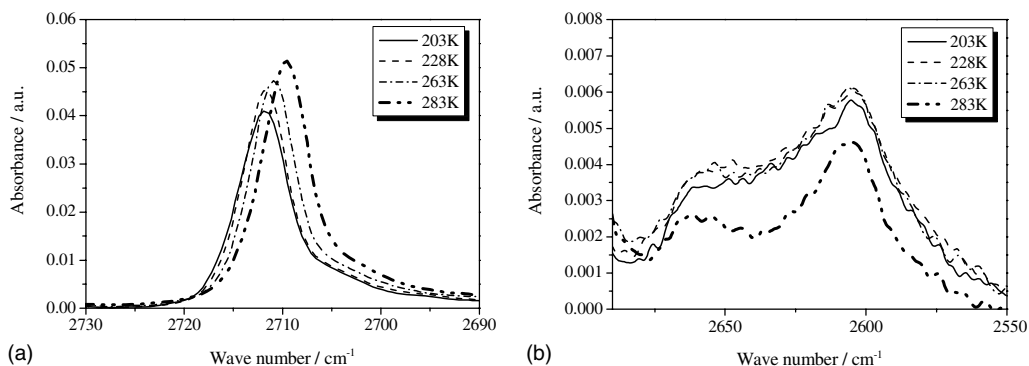


Fig. 5. FT-IR spectra of Li_2O after deuterium ion irradiation ($1.0 \times 10^{22} \text{ D m}^{-2}$) at various temperature in the wave number of (a) 2730–2690 cm^{-1} , the area of LiOD phase peak; and (b) 2690–2550 cm^{-1} , the area of other O–D bond peak.

between 2500 and 2700 cm^{-1} of the spectrum irradiated at 228 K. To understand in more detail the behavior, the area related to O–D bonds in/on Li_2O was grouped into two regions, namely the LiOD related region at the wave number of 2710 cm^{-1} (solid circles), and the other region including O–D bonds affected by the defects at the wave number of 2605 cm^{-1} , a surface O–D bond with several adjacent O–D bonds at around 2660 cm^{-1} and the broad peak of 2700–2500 cm^{-1} (open circles). Figs. 3 and 4 show the changes of these two intensities as a function of the deuterium ion fluence at 323 and 228 K. It was found that, at 323 K, the LiOD phase peak quickly increased and was almost saturated at the fluence of $6 \times 10^{21} \text{ D m}^{-2}$. At 228 K, the production of LiOD phase was restrained in the beginning of the deuterium ion irradiation. However, the other area including the broad peak was increased quickly and almost saturated above a fluence of $2.0 \times 10^{21} \text{ D m}^{-2}$. After the saturation of the peak area without the LiOD phase peak, the LiOD phase peak has started to increase slowly. In the temperature dependence of the peak at 2710 cm^{-1} during the deuterium ion irradiation, the increasing rate of the peak intensity at 228 K was lower than that at 323 K. These results indicate that the formation of LiOD phase was restrained at 228 K compared to the experiment at 323 K. Therefore, the other chemical states of deuterium are considered to be stable in this low temperature region and to be unstable in RT. To determine the temperature dependence after the deuterium ion irradiation, the Li_2O sample was heated slowly up to 283 K. Fig. 5 shows the FT-IR spectra of the LiOD phase peak in Fig. 5(a) and the region of the other peaks obtained at each temperature in Fig. 5(b). Although the LiOD phase peak clearly increased on heating, the other O–D bonds have no change in this temperature range of 203–263 K. It indicates that some of the deuterium ions exist without forming O–D bonds in Li_2O at low temperature. As the temperature increased between 263 and 283 K, the LiOD phase increased and the other O–D bonds de-

creased. Therefore, the O–D bonds as the broad peak between 2700 and 2500 cm^{-1} are believed to change to the LiOD phase because of the low stability at 283 K.

These experimental results indicate that at low temperature, several states of the deuterium exist, which are unstable at RT, and they change to the LiOD phase as the temperature increases. The chemical state of the hydrogen isotopes depends on the sample temperature.

4. Conclusion

The hydrogen isotope behavior in Li_2O at low temperature was studied to clarify the fundamental behavior of hydrogen isotopes. The Li_2O sample was irradiated by 3 keV deuterium ions at about 228 K with flux of $1.3 \times 10^{17} \text{ D m}^{-2} \text{ s}^{-1}$ and fluence up to $1.0 \times 10^{22} \text{ D m}^{-2}$. It was found that three peaks at 2710, 2660, and 2605 cm^{-1} , and an abroad peak of 2700–2500 cm^{-1} , were observed. The formation of the LiOD phase was suppressed at the low temperature and the O–D bonds, which could not exist at RT because of the low stability, were formed in Li_2O . These O–D bonds with low stability change to the LiOD phase when the temperature is increased. It was concluded that the chemical states of hydrogen isotopes varied with the sample temperature during the deuterium ion irradiation.

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