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Observation of multiple O–D vibration peaks in Li_2O using FT-IR

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Abstract

In order to estimate the stabilities of various O–D states formed in Li_2O by 3 keV D_2^+ irradiation, heating experiments up to 453 K were conducted. The chemical states of O–D bonds were analyzed by FT-IR, and the variation of the intensities of the O–D bonds in various chemical states were studied individually. During the irradiation, two O–D states were mainly formed in the bulk: O–D bond existing as LiOD phase or that without forming the LiOD phase. As sample temperature increased, transition of the latter to the former was observed. The apparent activation energy for the decrease of the O–D bond without forming the LiOD phase was estimated to be 60 kJ/mol over the temperature range 320–362 K, and that existing as the LiOD phase was estimated to be 130 kJ/mol over 403–453 K.

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1. Introduction

Lithium oxide (Li_2O) is one of the candidate solid breeding materials for a fusion reactor. In the solid breeding material, radiation defects are expected to influence hydrogen isotope behavior; for example, H^+ could be reduced by combination with F centers [1]. Therefore, many studies have been devoted to understand the behavior of radiation defects in Li_2O, especially F centers [2] and Li colloids [3]. Generation, annihilation and aggregation behavior of these defects has been reported in various conditions. In the last ten years, additionally, quantum chemical calculation has contributed to understand the stability of hydrogen isotopes in Li_2O with or without interaction with vacancies [4,5]. However, the interaction of hydrogen isotopes with the radiation defects has not been sufficiently defined for lack of the experimental information on the atomic scale behavior of hydrogen isotopes.

Recently, we have conducted IR absorption analyzes of Li_2O during and after 3 keV D_2^+ irradiation to study the behavior of irradiated hydrogen isotopes in various chemical states [6]. Three peaks corresponding to various O–D stretching vibration were observed, and two of them were related to the O–D bonds in the bulk: (i) O–D bond existing as LiOD phase [7] and (ii) O–D bond without forming the LiOD phase and with interaction with vacancies [8]. In the present work, the Li_2O sample was heated up to 453 K after the 3 keV D_2^+ irradiation. The annealing behavior of these O–D states was analyzed, and the stability of them was discussed.

2. Experimental

A disk sample was cut from a Li_2O single crystal grown by the floating zone method [9]. The disk diameter was 8 mm and thickness 1 mm. In order to remove the impurities, such as LiOH and Li_2CO_3, the sample

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was annealed in a vacuum of 1×10^{-4} Pa at 973 K for one day. Subsequently, the sample was loaded into the IR absorption analysis system. The schematic drawing of this system was shown in Ref. [6]. This system consists of FT-IR (Mattson, Infinity Gold) with a MCT detector, an ion gun, a vacuum chamber, and a heating and cooling unit. An in-situ IR absorption analysis can be conducted under ion irradiation and pressure on the order of 10^{-6} Pa with the sample temperature controlled in the range 173–1173 K. Before a series of experiments, the sample was annealed again under pressure on the order of 10^{-6} Pa at 923 K until the IR absorption peaks related to –OH and –OD disappeared completely.

In this study, the sample was heated stepwise to 453 K after the 3 keV D_2^+ irradiation with the flux of 1.3×10^{17} ions $m^{-2}\,s^{-1}$ up to the fluence of 1.0×10^{22} ions m^{-2}, where the peaks corresponding to O–D bonds in the bulk had grown sufficiently. According to the result of TRIM calculations, the average doped depth of the 3 keV D_2^+ was 47 nm. The behaviors of irradiated deuterium ions during the irradiation have been described in Ref. [6].

To estimate the concentration of each type of O–D bond in the Li_2O sample, IR spectra obtained during the heating were converted to absorbance format using the spectrum before the ion irradiation as a reference. It is known that the intensity of the peak is proportional to the concentration of IR absorbing species. The intensity of the peak was evaluated using the Lorentz function after subtracting the appropriate background. The spectra were recorded with a range 1000–4000 cm^{-1}, a resolution of 2 cm^{-1} and scans of 2000, where enough S/N ratio was obtained to evaluate the intensity of the peak.

3. Results and discussion

During the stepwise heating from room temperature (RT) to 453 K, the intensity of the peak at 2605 cm^{-1} started to decrease at 320 K and almost disappeared at 362 K, and that at 2710 cm^{-1} started to decrease after the disappearance of the peak at 2605 cm^{-1} and had disappeared at 473 K. In the latter section, therefore, the decay of the peak at 2605 cm^{-1} is discussed over the temperature range 320–362 K, and that at 2710 cm^{-1} over 403–453 K.

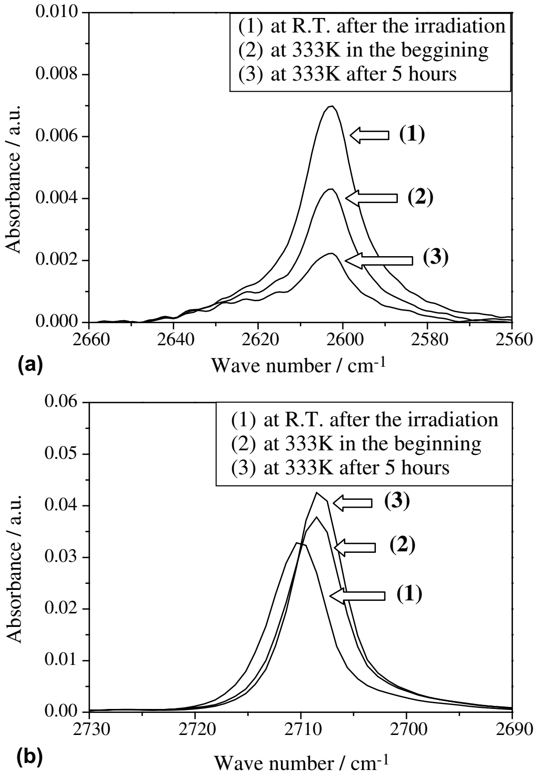

Fig. 1. Spectra of Li_2O after 3 keV D_2^+ irradiation in various conditions: (1) at RT; (2) at 333 K in the beginning of heating; (3) at 333 K after heating for 5 h. (a) Shows the peak at 2710 cm^{-1} corresponding to the O–D bond existing as the LiOD phase, and (b) the peak at 2605 cm^{-1} corresponding to the O–D bond without forming the LiOD phase after subtracting the appropriate background and the contribution of the surface O–D bond.

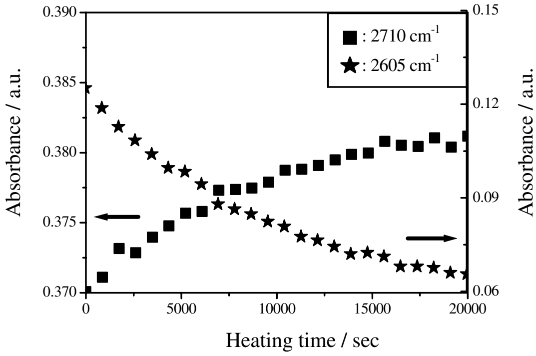

Fig. 2. Variations of the intensities of the peaks at 2710 and 2605 cm^{-1} as a function of heating time at 333 K.

Fig. 1 shows the variations of IR spectra for 3 keV D_2^+ irradiated Li_2O; (1) at RT just after the irradiation, (2) at 333 K in the beginning of heating and (3) at 333 K after heating for five hours. The peak shown in Fig. 1(a) is associated with the O–D bond without forming the LiOD phase at 2605 cm^{-1}, and that in Fig. 1(b) with the O–D bond existing as the LiOD phase at 2710 cm^{-1}. It was found that the intensity of the peak corresponding to O–D bond without forming the LiOD phase decreased on heating, and that of the O–D bond existing as the LiOD phase increased at the same time over 320–362 K. Fig. 2 describes the variations of the intensity of these peaks on heating. The decreasing behavior of the intensity of the peak at 2605 cm^{-1} was comparable with the increasing behavior of that at 2710 cm^{-1}. It shows that the O–D bond without forming the LiOD phase changed to the LiOD phase on heating. In the case of a measurement during deuterium ion irradiation, the formation of the O–D bond without forming the LiOD phase started to appear at a lower deuterium ion fluence than that of the O–D bond existing as the LiOD phase. This phenomenon was explained by taking into account the aggregation process of O–D bonds to form the LiOD phase [6]. The present observed transition of O–D bond without forming the LiOD phase to that existing as the LiOD phase at 333 K supports the formation process of LiOD phase by the aggregation of O–D bonds suggested in [6]. It should be mentioned that the peak shift of the O–D bond existing as the LiOD phase was found as show in Fig. 1(b). The shift is considered to be related to the expansion of the Li_2O crystal as the sample temperature increased. This phenomenon will be studied in detail in the near future.

In order to study the mechanism of the change of the O–D without forming the LiOD phase to that existing as the LiOD phase, the decrease of the intensity of the peak at 2605 cm^{-1} was shown in Fig. 3 with two fitted curves as functions of heating time: the broken and the solid curves are based on the assumption of the order of the reaction as first or second, respectively. The solid line seemed to be better fitted than the broken one. For the formation of the LiOD phase, two aggregation processes of O–D bonds were considered: (i) the O–D bonds without forming the LiOD phase combine with each other, and (ii) the O–D bond without forming the LiOD phase is absorbed by the LiOD phase. The reaction would be second order in the former case, and first order in the latter. Therefore, the former process may be dominant in the present experimental conditions. However, further studies are necessary to ensure this conclusion. The apparent activation energy for the disappearance of the O–D bond without forming the LiOD phase at 2605 cm^{-1} was estimated from the Arrhenius plots in Fig. 4 with an assumption of second order reaction. It was evaluated to be 60 kJ/mol over the temperature range 320–362 K.

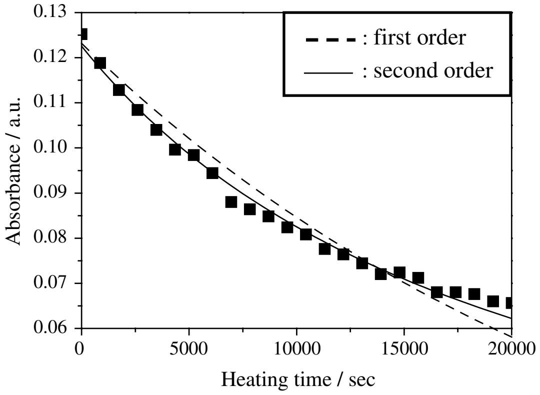

Fig. 3. Decreasing intensity of the peak at 2605 cm^{-1} at 333 K. The solid and the broken lines are fitted curves drawn with assumptions of second and first order reactions, respectively.

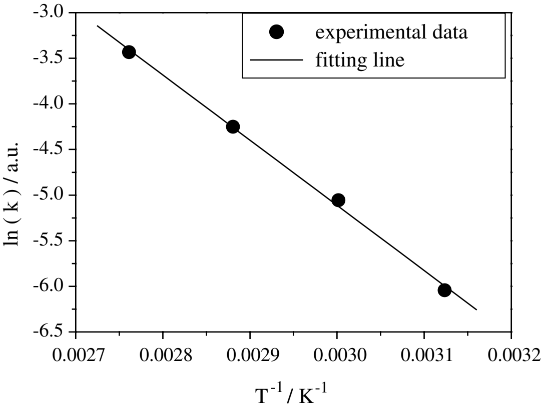

Fig. 4. Arrhenius plots for the decreasing intensity of the peak at 2605 cm^{-1} over the temperature range 320–362 K with the assumption of a second order reaction. Here, k is the reaction rate constant.

The intensity of the peak at 2710 cm^{-1} corresponding to the LiOD phase started to decrease after the disappearance of the O–D bond without forming the LiOD phase. The decrease of the intensity of the peak at 2710 cm^{-1} over the temperature range 403–453 K is described in Fig. 5. The fitted curves were drawn with the assumption of a first order reaction. In the case of LiOD crystal, not the LiOD phase, the apparent activation energy has been estimated to be 120 kJ/mol over the

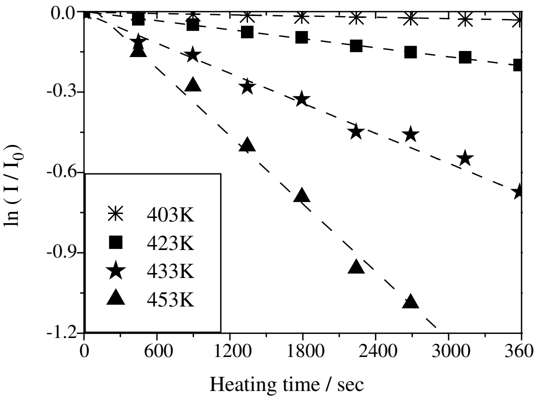

Fig. 5. Decreasing intensities of the peak at 2710 cm^{-1} at 403, 423, 433 and 453 K. The fitted curves were drawn with the assumption of a first order reaction. Here, I/I_0 indicates the normalized intensity.

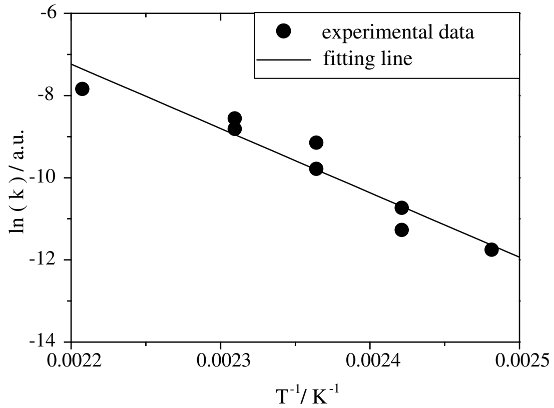

Fig. 6. Arrhenius plots for the decreasing intensity of the peak at 2710 cm^{-1} over the temperature range 403–453 K with the assumption of a first order reaction. Here, *k* is the reaction rate constant.

temperature range 530–690 K using the mass spectroscopic method [10]. The decomposition reaction was considered to be a first order reaction in the quantity of released water, and the decomposition on the surface would be the rate determining process [10]. In the present study, therefore, the apparent activation energy for the decrease of the LiOD phase was evaluated with an assumption of a first order reaction. In this assumption, the apparent activation energy was estimated from the Arrhenius plots in Fig. 6 to be 130 kJ/mol over the temperature range 403–453 K. This value was comparable with the reported value of 120 kJ/mol for the LiOD crystal. However, the decomposition temperature was quite low in the case of the LiOD phase compared with that of the LiOD crystal. In the reported work [10], the amount of D_2O produced by the thermal decomposition of the LiOD crystal was measured by the mass spectroscopic method. On the other hand, in the present work, not only the decomposition of the LiOD phase on the surface, but also the interface reaction between the LiOD phase and the Li_2O crystal were analyzed by the IR absorption method. The contribution of the decomposition of the LiOD phase at the interface could be larger than that on the surface, since the decomposition on the surface should have hardly occurred over 403–453 K. It is concluded that the observed decrease of the LiOD phase over such low temperature range could be attributed to the interface reaction between the LiOD phase and the Li_2O crystal.

4. Conclusions

Heating experiments were conducted to estimate the stability of O–D states in Li_2O formed by 3 keV D_2^+ irradiation. The behavior of two O–D states, namely O–D bond existing as LiOD phase and O–D bond without forming the LiOD phase, were analyzed using FT-IR and the following information was obtained.

(i) The O–D bond without forming the LiOD phase, corresponding to the IR absorption peak at 2605 cm^{-1}, changed to the O–D bond existing as the LiOD phase, at 2710 cm^{-1}, as the sample temperature increased over the temperature range 320–363 K. The decreasing intensity of the peak at 2605 cm^{-1} and the increasing intensity of that at 2710 cm^{-1} were comparable.
(ii) In the case of the O–D bond without forming the LiOD phase, the apparent activation energy for the decrease of this O–D state was estimated to be 60 kJ/mol over the temperature range 320–362 K with the assumption of a second order reaction.
(iii) As for the O–D bond existing as the LiOD phase, the apparent activation energy of the decrease of this O–D state was evaluated to be 130 kJ/mol over 403–453 K with the assumption of a first order reaction.

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