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IR observation on O–D vibration in $LiNbO_3$ and $LiTaO_3$ single crystal irradiated by 3 keV D_2^+

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ABSTRACT

The behavior and existence states of deuterium irradiated into $LiNbO_3$ and $LiTaO_3$ single crystals were studied by *in situ* FT-IR observations on multiple O–D vibration peaks and by TDS on the desorption behavior of deuterium. Two O–D vibration peaks were observed in both $LiNbO_3$ and $LiTaO_3$, one at 2610–2615 cm^{-1} and the other at 2560–2570 cm^{-1}. The former O–D vibration was attributed to $-OD^-$ affected by Nb defect in $LiNbO_3$ or Ta defect in $LiTaO_3$. For attribution of the latter O–D vibration, two candidates remained, $-OD^-$ affected by Li vacancy and $-OD^-$ of interstitial D^+. By heating after the ion irradiation, the irradiated deuterium was mainly desorbed as hydrogen molecular forms (D_2 and HD). The $-OD^-$ affected by Nb defect in $LiNbO_3$ or Ta defect in $LiTaO_3$ had a higher desorption temperature than the other $-OD^-$s. The two materials showed similar results in the existence states and the desorption behavior of irradiated D^+, although some differences were observed due to more formation of Nb defect in $LiNbO_3$ than Ta defect in $LiTaO_3$ by displacement. It was indicated that the release temperature of hydrogen isotopes is heightened by the influence of M defect in ternary lithium oxides (Li_xMO_y).

1. Introduction

Ternary lithium oxides such as Li_2TiO_3 and Li_4SiO_4 are regarded as candidate breeders in solid blanket concepts [1]. Diffusivity of tritium in ternary lithium oxides is one important parameter for the release process of tritium from solid breeders. However, in previous studies, several discrepancies and uncertainties arose on tritium diffusivities evaluated in ternary lithium oxides [2–4], probably due to surface processes or influences of radiation defects. Since trapping of tritium by various irradiation defects is considered to affect the diffusion of tritium, studies on the interactions between hydrogen isotopes and irradiation defects can be contributed to evaluation of tritium diffusivity in reactor conditions.

Hydrogen isotopes in metal oxides are basically attracted by a neighboring oxygen ion to form $-OH^-$ [5]. The influences by various irradiation defects are reflected by different O–H vibration peaks. Therefore, observation of these vibration peaks by Fourier transform infrared spectroscopy (FT-IR) can be applied for understanding on the interactions between hydrogen isotopes and irradiation defects.

The deuterium ion irradiation introduces hydrogen isotopes and radiation defects into the sample simultaneously, and thus facilitates analysis of their interaction [6–8]. In our previous work, O–D vibration peaks in $LiAlO_2$ were observed by *in situ* IR absorption spectroscopy during irradiation with 3 keV D_2^+ at room temperature [9]. Consequently, multiple IR absorption peaks related to O–D stretching vibrations were observed in $LiAlO_2$, mainly at 2650 cm^{-1} (O–D_α), 2600 cm^{-1} (O–D_β), and 2500 cm^{-1} (O–D_γ). The O–D_α was attributed to the surface $-OD^-$. Although attributions of O–D_β and O–D_γ have not been completed, one of them seemed to correspond to an $-OD^-$ affected by Al defect in $LiAlO_2$ [9]. Hence, the present study is designed to clarify the influence of M defect (M indicates an element other than lithium and oxygen in ternary lithium oxides, namely Al in $LiAlO_2$, Nb in $LiNbO_3$ and Ta in $LiTaO_3$) on the behaviors of hydrogen isotopes in ternary lithium oxides (Li_xMO_y).

For this purpose, influences by other factors such as crystal structure, grain size and particle size should be avoided. It is known that $LiNbO_3$ and $LiTaO_3$ possess the same crystal structure (crystal system: *trigonal*, space group: *R3c*), and have similar material property except a significant difference in the atomic weight of M: niobium 92.906, tantalum 180.948. Therefore use of $LiNbO_3$ and $LiTaO_3$ single crystals is an appropriate way for the study on the influence of M defect on the behavior of hydrogen isotopes in ternary lithium oxides. Thermal desorption spectroscopy (TDS) with

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combination of ion implantation technology has been applied in the study on the behavior of hydrogen isotopes in PFM [10,11] and tritium breeding materials [8,9] for fusion reactor. Therefore the observation of deuterium released from D_2^+-irradiated $LiNbO_3$ and $LiTaO_3$ single crystals by TDS should be helpful to the present study.

The following experiments were performed for $LiNbO_3$ and $LiTaO_3$ single crystal plates in the present paper: (i) *in situ* IR absorption analyses during 3 keV D_2^+ irradiation; (ii) *in situ* IR absorption analysis during stepwise heating after the ion irradiation; and (iii) Thermal Desorption Spectroscopy (TDS) during isochronal heating after the ion irradiation. Experiment (i) was designed to compare O–D vibration peaks between D_2^+-irradiated $LiNbO_3$ and $LiTaO_3$ and to understand the existence states of irradiated deuterium. Experiments (ii) and (iii) were carried out to establish a correspondence between the existence states and the release behavior of irradiated deuterium. This correspondence can help us to further understand the influence of M defect on the release behavior of hydrogen isotopes from ternary lithium oxides.

2. Experimental

Single crystal plates of $LiNbO_3$ and $LiTaO_3$ ($10 \times 10 \times 0.5$ mm, 99.99% purity, $\langle 001 \rangle$ orientation, MTI Corp.) were used as samples. In order to remove impurities induced by exposure to air, such as hydrate and carbonate, the samples were annealed at 800 K in a vacuum lower than 5×10^{-5} Pa for more than 20 h after introduction into an IR absorption analysis system.

The experimental system consisted of FT-IR (Mattson, Infinity Gold) with an MCT detector, a mirror for the diffuse reflectance method, a quadruple mass spectrometer (QMS), an ion gun, a vacuum chamber, a heating unit, a Faraday cup, and a cover to prevent ion irradiation on the molybdenum sample holder. A schematic drawing of the system can be seen in Ref. [6]. The samples were irradiated with 3 keV D_2^+ at a flux of $1.6 \times 10^{17}\ m^{-2}\ s^{-1}$ up to the fluence level of $3 \times 10^{21}\ m^{-2}$ at room temperature. The irradiation was directed towards the sample surface at an angle of 45°. A temperature rise induced by ion irradiation was less than 20 K.

Isochronal heating experiments were conducted with a rate of about $20\ K\ min^{-1}$ up to 800 K after ion irradiation. IR absorption spectra and TDS spectra were acquired simultaneously during the isochronal heating. The chemical forms and the amounts of desorbed deuterium were determined by QMS.

3. Results

3.1. IR spectra during 3 keV D_2^+ irradiation

The *in situ* IR spectra were obtained for $LiNbO_3$ during the irradiation with the flux of $1.6 \times 10^{17}\ D_2^+\ m^{-2}\ s^{-1}$ as shown in Fig. 1. Two O–D vibration peaks were mainly observed at $2615\ cm^{-1}$ (termed as O–D_a) and at $2565\ cm^{-1}$ (termed as O–D_b). The *in situ* IR spectra were also obtained for $LiTaO_3$ under the same irradiation condition as shown in Fig. 2. These IR spectra are compared in Fig. 3 with peak fitting results (here a broad peak from 2400 to $2550\ cm^{-1}$ was neglected because it seemed to consist of multiple IR absorption peaks which might be due to impurity or environment gas). Although the peak positions are comparable, it is clear that the relative intensity of the two peaks is different between $LiNbO_3$ and $LiTaO_3$, as expressed by

$$\left(\frac{I_{O-D_a}}{I_{O-D_b}}\right)_{LiNbO_3} > \left(\frac{I_{O-D_a}}{I_{O-D_b}}\right)_{LiTaO_3}, \tag{1}$$

where I_{O-D_a} indicates the peak intensity of O–D_a and I_{O-D_b} of O–D_b.

3.2. TDS after the ion irradiation

TDS experiments after the ion irradiation showed that most deuterium (more than 90%) was desorbed as hydrogen molecular forms (D_2 and HD) in both $LiNbO_3$ and $LiTaO_3$. Desorption curves of deuterium as hydrogen molecular forms was dealt by peak fitting as shown in Fig. 4 (here a small desorption peak between 550 K and 650 K was neglected because it seemed not to be observed repeatedly and might be from chamber materials). Based on the peak fitting results, desorption of deuterium as hydrogen molecular forms consisted of two desorption peaks at 450 K (termed as peak-l) and 525 K (termed as peak-h). In comparison of TDS between $LiNbO_3$ and $LiTaO_3$ (Fig. 4), the following expression was obtained as

$$\left(\frac{D_{peak\text{-}h}}{D_{peak\text{-}l}}\right)_{LiNbO_3} > \left(\frac{D_{peak\text{-}h}}{D_{peak\text{-}l}}\right)_{LiTaO_3}, \tag{2}$$

where $D_{peak\text{-}h}$ indicates the amount of deuterium released in peak-h and $D_{peak\text{-}l}$ in peak-l.

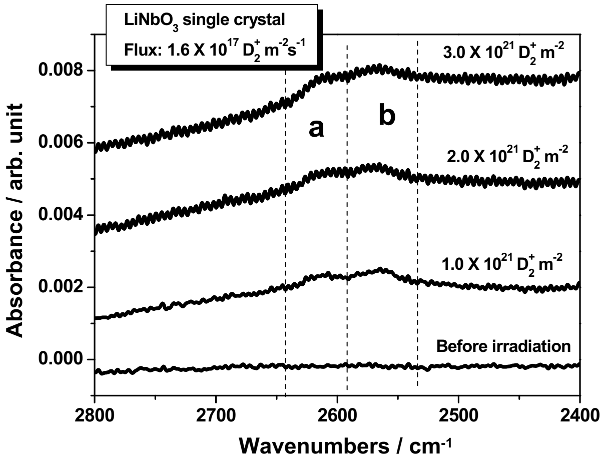

Fig. 1. IR spectra of $LiNbO_3$ single crystal plate during the irradiation with the flux of $1.6 \times 10^{17}\ D_2^+\ m^{-2}$.

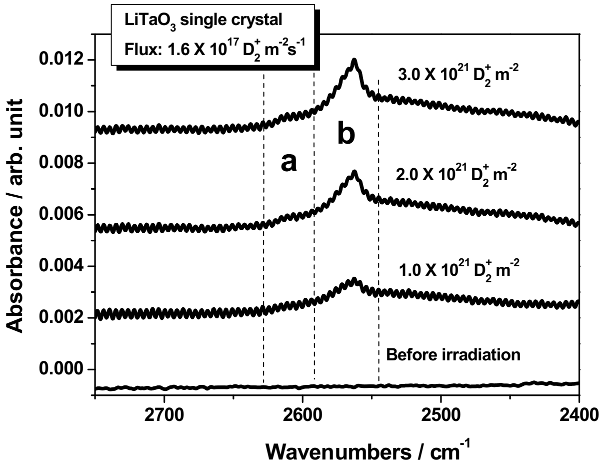

Fig. 2. IR spectra of $LiTaO_3$ single crystal plate during the irradiation with the flux of $1.6 \times 10^{17}\ D_2^+\ m^{-2}$.

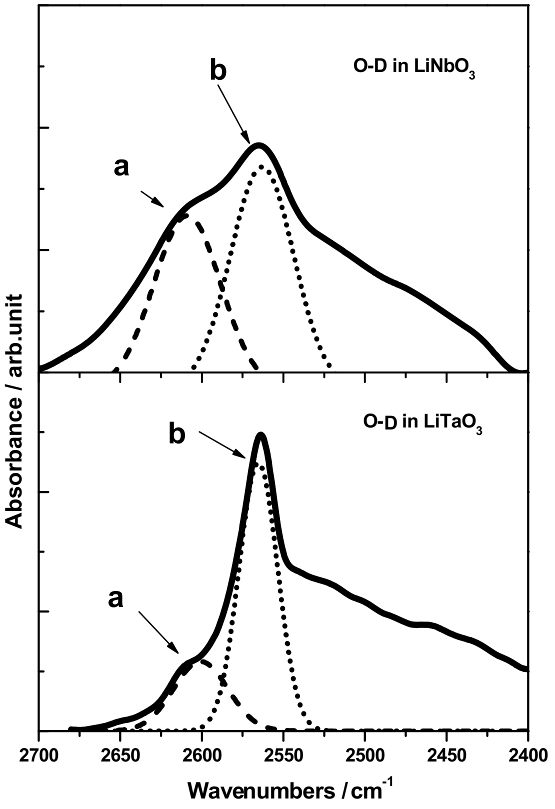

Fig. 3. Comparison of O–D vibration peaks in $LiNbO_3$ and $LiTaO_3$.

3.3. IR spectra during heating after the ion irradiation

The IR spectra of D_2^+-irradiated $LiNbO_3$ during heating at different temperatures are shown in Fig. 5. In comparison of spectra at 300 K and 500 K, O–D_b decreased from 300 to 500 K while O–D_a was hardly changed. From 500 to 650 K, both O–D_a and O–D_b decreased and disappeared above 650 K. The variation of peak intensities of O–D_a and O–D_b in D_2^+-irradiated $LiNbO_3$ are shown as a function of heating temperature in Fig. 6. O–D_a decreased from 480 K and O–D_b decreased from 380 K. Peak intensities in D_2^+-irradiated $LiTaO_3$ during heating are also shown in Fig. 7. The intensity of O–D_b in $LiTaO_3$ started to decrease from 380 K, which was the same to that in $LiNbO_3$. Since the fraction of deuterium as O–D_a in $LiTaO_3$ was little, the change of the intensity of O–D_a was unclear in $LiTaO_3$.

4. Discussion

4.1. Correspondence between –OD^- states and D_2 desorption

Table 1 summarizes the experimental results given in the Section 3. In IR spectra obtained during D_2^+ irradiation, two O–D vibration peaks (O–D_a and O–D_b) were observed in both $LiNbO_3$ and $LiTaO_3$. As the peak positions of the two peaks were comparable between $LiNbO_3$ and $LiTaO_3$, O–D_a and O–D_b in $LiNbO_3$ could have the same origins with those in $LiTaO_3$. However, the intensity ratio between the two O–D peaks in $LiNbO_3$ was different from that in $LiTaO_3$ as described by the expression (1).

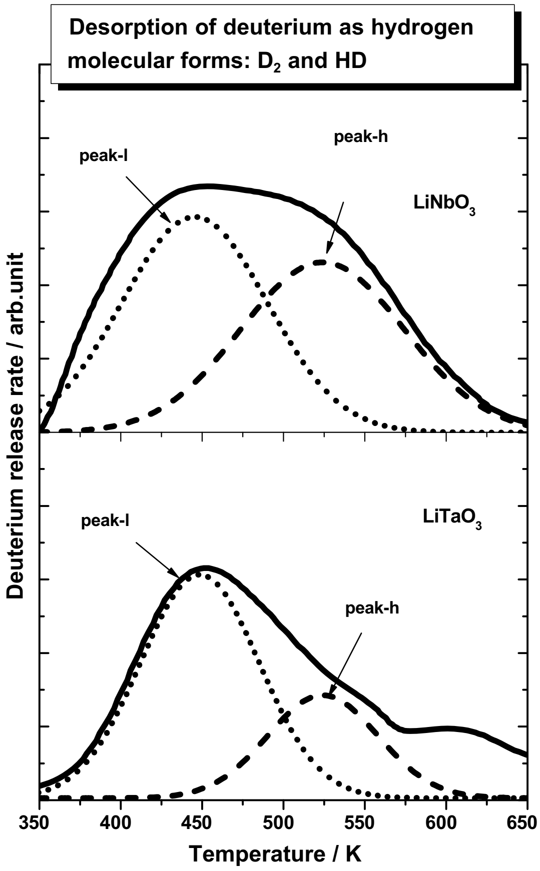

Fig. 4. Comparison of deuterium desorbed as hydrogen molecular forms in $LiNbO_3$ and $LiTaO_3$.

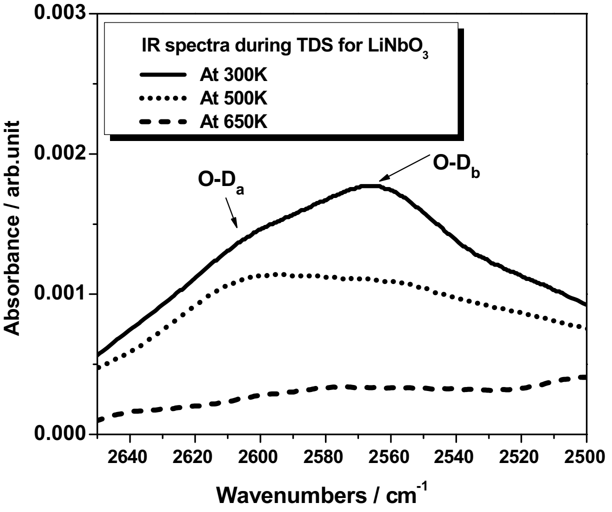

Fig. 5. IR spectra of irradiated $LiNbO_3$ single crystal plate at different temperatures.

In analogous with the IR observation, two D_2 desorption peaks ($D_{peak\text{-}l}$ and $D_{peak\text{-}h}$) were obtained in TDS spectra after the D_2^+ irradiation. As the desorption temperatures of the two D_2 were comparable between $LiNbO_3$ and $LiTaO_3$, the origins of $D_{peak\text{-}l}$ and $D_{peak\text{-}h}$ in $LiNbO_3$ could be the same with those in $LiTaO_3$, respectively. However, again the ratio of desorption amount between the two D_2 peaks in $LiNbO_3$ was different from that in $LiTaO_3$ as described by expression (2). The correspondence between expressions (1) and (2) indicates that O–D_a correlates with $D_{peak\text{-}h}$, and O–D_b with $D_{peak\text{-}l}$ (Table 1).

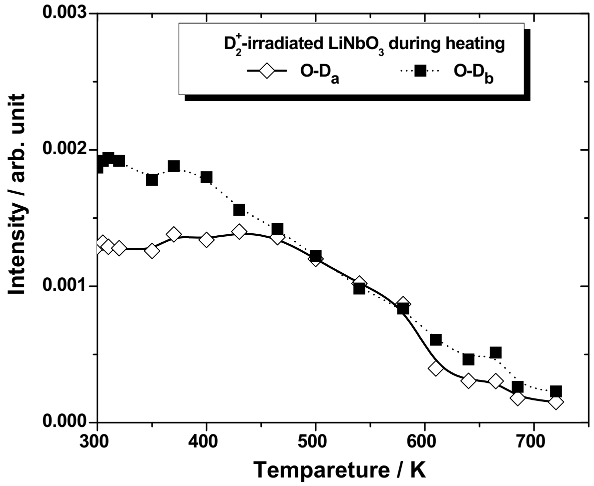

Fig. 6. Intensity of O–D_a and O–D_b in an irradiated $LiNbO_3$ single crystal plate as a dependence of heating temperature.

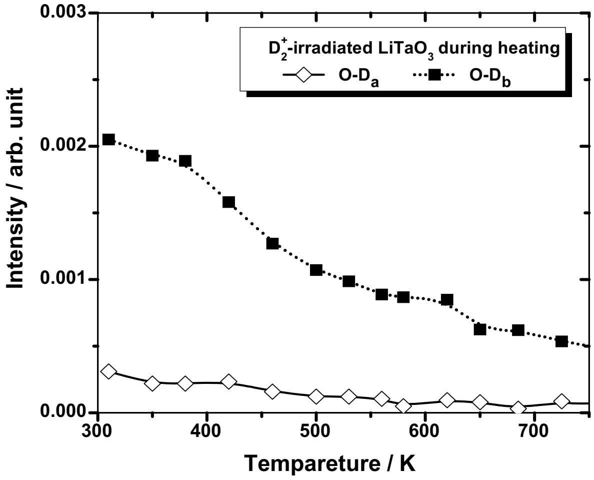

Fig. 7. Intensity of O–D_a and O–D_b in an irradiated $LiTaO_3$ single crystal plate as a dependence of heating temperature.

In the IR spectra obtained during heating (Fig. 5), O–D_b started to decrease prior to O–D_a. This observation also supports the correspondences between O–D_a and $D_{peak\text{-}h}$ and between O–D_b and $D_{peak\text{-}l}$.

The correspondence between O–D vibration peaks and D_2 desorption peaks implied that the deuterium existing as $-OD^-$ can be desorbed as hydrogen molecular forms (D_2 and HD). It has been considered that deuterium existing as $-OD^-$ is basically desorbed as water forms (D_2O and HDO) [1], and that the desorption of deuterium as D_2 is due to the existence of non-O–D states such as D^0 and D^- [9,12]. Therefore another mechanism on desorption behavior of hydrogen isotopes is needed to explain the present results. One possible reason of D_2 desorption is strong reduction of the surface due to selective sputtering of O^{2-} by D^+ irradiation, as observed in Li_2TiO_3 by Ar^+ irradiation [13]. This will be discussed in the future work.

4.2. Attributions of O–D_a and O–D_b

It has been reported that both O–D_a and O–D_b were observed when $LiNbO_3$ single crystal was heated in D_2O vapor at 625–750 K after neutron irradiation [14]. In this case, the formation of O–D_a and O–D_b has been ascribed to the isotope substitution between tritium induced by neutron irradiation and deuterium in D_2O. O–D_b has been indicated by a sharp and predominant peak while O–D_a only by a very small peak [14]. On the other hand, if neutron irradiation was not conducted and deuterium was thermally introduced from D_2O vapor, only O–D_b was observed in $LiNbO_3$ [15] and $LiTaO_3$ [16,17]. The fact that O–D_a was not observed in un-irradiated $LiNbO_3$ and $LiTaO_3$ in these experiments indicates that O–D_a correlates with certain irradiation defects.

In order to make attribution of O–D_a, we considered the defect formation in $LiNbO_3$ and $LiTaO_3$. As for the threshold displacement energy, $LiNbO_3$ and $LiTaO_3$ could have a comparable value, because they have the same crystal structure and the similar ionic state. Therefore it is considered that the number of defects in $LiNbO_3$ and in $LiTaO_3$ depends mainly on energy gains of constituent atoms by collision with 3 keV D_2^+.

The elastic collision approximations are useful to estimate energy gains by collision qualitatively, although estimated values are corresponding to the maximum energy gain due to neglect of the electronic energy loss. In this approximation, the obtained kinetic energies of Li, Nb and Ta by collision with 1.5 keV D (corresponding to 3 keV D_2^+) are 1037 eV, 124 eV and 65 eV, respectively. The large difference of the energy gain between Nb and Ta suggests that the number of Nb defect induced by irradiation in $LiNbO_3$ is significantly larger than that of Ta defect in $LiTaO_3$, while that of Li defects and O defects could be in the same level between the two materials. In the experiments, the intensity ratio of O–D_a to O–D_b in $LiNbO_3$ was higher than that in $LiTaO_3$ as shown in expression (1). Hence O–D_a was attributed to $-OD^-$ affected by Nb defect in $LiNbO_3$ or Ta defect in $LiTaO_3$. As O–D_a was thought to be $-OD^-$ affected by a radiation defect as discussed above, this attribution is reasonable.

For O–D_b, two candidates remain: $-OD^-$ of interstitial D^+ and $-OD^-$ affected by Li^+ vacancy. Different from O–D_a, O–D_b was observed even in experiments without irradiation [15–17], which suggest that the irradiation defects are not required for its formation. It has been reported that the proton of the O–H bond corresponding to O–D_b lies only 0.02 nm below the oxygen plane (along the *c* axis) at a distance of 0.1 nm from the corresponding oxygen atom [18]. Based on this experimental observation, it has been suggested that the hydrogen atom of O–D_b lies on the interstitial site not substitutional site [19,20].

Table 1
Correspondence between O–D vibration peaks and desorption states of deuterium as D_2 in $LiNbO_3$ and $LiTaO_3$ single crystal samples

	Desorption of D_2 T_{peak}: desorption peak temperature $D_{peak\text{-}x}$: amounts of deuterium desorbed as peak-x	O–D vibration peaks $T_{annihilation}$: temperature for annihilation
$LiNbO_3$	Peak-l: $T_{peak} = 450$ K Peak-h: $T_{peak} = 525$ K	O–D_b: $T_{annihilation}$ from 380 K O–D_a: $T_{annihilation}$ from 480 K
$LiTaO_3$	Peak-l: $T_{peak} = 450$ K Peak-h: $T_{peak} = 525$ K	O–D_b: $T_{annihilation}$ from 380 K O–D_a: not clear
Comparison	$(\frac{D_{peak\text{-}h}}{D_{peak\text{-}l}})_{LiNbO_3} > (\frac{D_{peak\text{-}h}}{D_{peak\text{-}l}})_{LiTaO_3}$	$(\frac{I_{O-D_a}}{I_{O-D_b}})_{LiNbO_3} > (\frac{I_{O-D_a}}{I_{O-D_b}})_{LiTaO_3}$

However, interstitial H^+ and H^+ substitutional for Li^+ are similar in their electronic structures and in the distance between a hydrogen atom and an oxygen atom, according to quantum chemical calculations for Li_2O [21]. The main difference between the two states is that substitutional H^+ is neighboring to Li vacancy while interstitial H^+ not. Moreover $LiNbO_3$ has a tendency to non-stoichiometry such as [Li]/[Nb] < 1 [22], and thus Li vacancies exist even without irradiation. Therefore at present it is difficult to determine whether O–D_b is due to $–OD^-$ affected by Li vacancy or $–OD^-$ of interstitial D^+. More supportive evidence would be needed for the attribution of O–D_b.

4.3. Influence of M defect on the behavior of hydrogen isotopes

Although the assignment of O–D_b has not been completed, the O–D_a having higher vibration frequency was attributed to $–OD^-$ affected by M (Ta^{5+} or Nb^{5+}) defect. This $–OD^-$ was annihilated in IR spectra at higher temperatures and was released at higher temperatures than the other $–OD^-$ states. These results indicate that M defect attracts hydrogen isotopes strongly and heightens its release temperature in ternary lithium oxides (Li_xMO_y). Therefore the influence of M defect should be considered to estimate tritium release rate under irradiation conditions.

5. Conclusions

The behavior and existence states of deuterium irradiated into $LiNbO_3$ and $LiTaO_3$ single crystal were studied by *in situ* FT-IR observations on multiple O–D vibration peaks and by TDS on the desorption behavior of deuterium. Two O–D vibration peaks at 2610–2615 cm^{-1} (O–D_a) and at 2560–2570 cm^{-1} (O–D_b) were observed in both $LiNbO_3$ and $LiTaO_3$. The fraction of deuterium existing as O–D_a in $LiNbO_3$ was higher than that in $LiTaO_3$. O–D_a has been attributed to $–OD^-$ affected by a defect of Ta^{5+} or Nb^{5+}. For attribution of O–D_b two candidates remained, $–OD^-$ affected by Li^+ vacancy and $–OD^-$ of interstitial D^+. By heating after the ion irradiation, the irradiated deuterium was mainly desorbed as hydrogen molecular forms (D_2 and HD). The $–OD^-$ affected by Nb defect in $LiNbO_3$ or Ta defect in $LiTaO_3$ had a higher desorption temperature than the other $–OD^-$s. The two materials showed similar results in the existence states and the desorption behavior of irradiated D^+, although some differences were observed due to more formation of Nb defect in $LiNbO_3$ than Ta defect in $LiTaO_3$ by displacement. It was indicated that the release temperature of hydrogen isotopes is heightened by the influence of M defect in ternary lithium oxides (Li_xMO_y). Therefore the influence of M defect should be considered to estimate tritium release rate under irradiation conditions.

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