First-Principles Study of Tritium Diffusion in the Li$_3$TaO$_4$ Crystal

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ABSTRACT: Li$_3$TaO$_4$ with a high melting point, good thermal stability, and higher lithium content has become a possible choice for breeder materials, which have potential applications in future fusion reactors. Perfect and defect crystal models of Li$_3$TaO$_4$ are set up, and all of the tritium-diffusion pathways have been studied by the first-principles method. The activation energy barriers of different diffusion pathways are calculated and analyzed considering the pathway length and tritium–oxygen interactions. The obtained minimum energy barrier for tritium diffusing in the perfect Li$_3$TaO$_4$ crystal is only 0.34 eV. The minimum energy barrier is less than 0.72 eV when tritium diffuses in the defect Li$_3$TaO$_4$ crystal in the presence of a lithium vacancy. Finally, the diffusion coefficients of tritium in the Li$_3$TaO$_4$ crystal are calculated, which further confirm that it is easy for tritium to escape from the trap of the lithium vacancy and diffuse in the crystal. Such a tritium-diffusion behavior is in favor of the tritium-release process of the Li$_3$TaO$_4$ crystal and could provide theoretical guidance for the future applications of Li$_3$TaO$_4$ materials.

1. INTRODUCTION

Lithium ceramic materials have attracted much attention for their potential applications as blanket materials in the nuclear fusion reactor, mainly due to their favorable properties such as high melting temperatures, low chemical reactivity, and high lithium (Li) densities.1–4 A number of lithium ceramic materials including Li$_2$O, Li$_2$SiO$_4$, Li$_2$TiO$_3$, Li$_2$ZrO$_3$, and LiAlO$_2$ have been investigated both theoretically and experimentally.5–11 In recent years, LiTaO$_3$ has become one of the potential ceramic breeder materials because of its high melting point and high thermal conductivity.12,13 As we know, crystalline LiTaO$_3$ is an outstanding material for its unique optical and ferroelectric properties, which has been studied systematically and used in many fields.14,15 In 2005, Naranjo et al. have found that the deuterium–deuterium (D–D) fusion reaction could be generated by gently heating the LiTaO$_3$ crystal in a deuterated atmosphere.12 It has been predicted that LiTaO$_3$ may have a higher tritium release rate than Li$_2$SiO$_4$ and Li$_2$TiO$_3$, according to the study of the behaviors of hydrogen isotopes in Li$_2$TaO$_3$.13 However, the lithium density is quite low in LiTaO$_3$, which limits its practical application as a blanket material. Therefore, Li$_3$TaO$_4$ with a higher Li content has become a possible choice as a blanket material due to its high melting point and good thermal stability.

Current studies on Li$_3$TaO$_4$ mainly include its crystal structure,16,17 and fabrication.18–20 Considering its potential application as a blanket material, the tritium-diffusion behavior in the Li$_3$TaO$_4$ crystal is essential and important to understand the tritium-release process. Besides, the tritium-release behavior is affected by various irradiation-induced defects, especially the lithium vacancy, because lithium atoms are constantly knocked out of their positions to generate tritium under irradiation. Several tritium-diffusion behaviors have been studied for Li$_2$SiO$_4$, Li$_2$TiO$_3$, Li$_2$ZrO$_3$, and LiAlO$_2$ crystals, and the activation energies predicted by related experiments and theoretical works normally range from 0.59 to 1.55 eV.21–27 However, there is no reported theoretical and experimental work on the tritium-diffusion properties of the Li$_3$TaO$_4$ crystal so far.

In this work, a comprehensive first-principles study of tritium diffusion in the Li$_3$TaO$_4$ crystal is presented. The perfect crystal model and the defect crystal model are set up and considered, respectively. The energy barrier and diffusion pathway of tritium in Li$_3$TaO$_4$ are calculated and analyzed to explain the tritium-diffusion process. Such theoretical results of tritium diffusion in the Li$_3$TaO$_4$ crystal are of prime importance for the understanding of the tritium behavior in the release process, which provides a theoretical guide for the design of the tritium breeding blankets.

2. THEORETICAL MODEL AND METHODS

In our study, according to the related experimental parameters, a 2 × 1 × 1 supercell of Li$_3$TaO$_4$ was employed, and then its geometry was optimized using density functional theory (DFT) calculations. The calculations have been performed by the Vienna ab initio simulation package (VASP).28,29 The projector augmented-wave (PAW) method30 and generalized gradient approximation (GGA) of Perdew–Burke–Ernzerhof are considered as basis.
were implemented. Convergence tests were conducted to determine the energy cutoff of the plane-wave basis and the k-point grid. Then, the plane-wave cutoff energy was set as 500 eV, and the geometry optimization was performed with the 2 × 2 × 2 Monkhorst–Pack k-point grid. Our benchmark calculations indicate that the error of total energy arising from this k-point sampling is less than 0.003 eV/Å. All tritium (T) atoms were treated as hydrogen atoms as they present the same electronic properties within DFT calculations.

Besides, the formation energy \( E_f(V_{Li}) \) for the defect model of Li₃TaO₄ is defined as follows \(^{32,33} \):

\[
E_f(V_{Li}) = E_{tot}(V_{Li}) - E_{tot}(Li_3TaO_4) + E_{Li-metal} + (E_f + E_v + \Delta V)
\]

\( E_{tot}(V_{Li}) \) is the total energy derived from a supercell containing the defect of a neutral Li vacancy, \( E_{tot}(Li_3TaO_4) \) is the total energy for the perfect crystal using an equivalent supercell, and \( E_{Li-metal} (\sim 3.61 \text{ eV}) \) is the mean atom energy of the Li metal. \( E_f \) is the Fermi level, referenced to the valence-band maximum (VBM, \( E_f \)) in the bulk, and \( \Delta V \) is the correction term to align the reference potential in our defective supercell with that in the perfect bulk.

The formation energy \( E_f(T_{Li}) \) of a tritium atom adsorbed in a neutral Li vacancy, namely the adsorption energy, is defined similarly to \( E_f(V_{Li}) \):

\[
E_f(T_{Li}) = E_{tot}(T_{Li}) - E_{vac} + E_T + (E_f + E_v + \Delta V)
\]

\( E_{tot}(T_{Li}) \) is the total energy of a Li₃TaO₄ supercell with tritium adsorbed in the Li vacancy, and \( E_{vac} \) is the total energy of an equivalent Li₃TaO₄ supercell with a Li vacancy. \( E_T \) is the chemical potential of a tritium atom (\(-1.12 \text{ eV}\)). The rest of the items are identical to the equation of \( E_f(V_{Li}) \). Because our studied defect is a neutral vacancy and the length of the supercell is relatively large (\( \approx 10 \text{ Å} \)), it is noted that the \( \Delta V \) values in the above two equations are actually neglected in our simulations.

Based on the above adsorption properties, the energy barriers of different diffusion pathways are further calculated with the climbing image nudged elastic band (NEB) scheme.\(^{34-36}\) When the length of the diffusion path is less than 2 Å, we use five images to ensure the calculation accuracy of the energy barriers and increase to seven images when the length is more than 2 Å.

3. RESULTS AND DISCUSSION

\( \beta \)-Li₃TaO₄ is a monoclinic crystal within the C2/c space group. Each primitive cell contains 64 atoms of 24 lithium (Li) atoms, 8 tantalum (Ta) atoms, and 32 oxygen (O) atoms, whose structure is presented in Figure 1. The labels of different colors listed on the right of Figure 1 correspond to the different types of atoms, respectively. It is noted that the blue tritium atoms in Figure 1 present the diffusion pathway, which will be discussed in the next section. As shown in Figure 1, every Li atom or Ta atom bonds with the neighboring six oxygen atoms, while each O atom bonds with the neighboring six atoms, which include four Li atoms and two Ta atoms or five Li atoms and one Ta atom. Initially, we relax the perfect crystal Li₃TaO₄ model, and obtain the lattice parameters of \( a = 8.5665 \text{ Å}, b = 8.5607 \text{ Å}, c = 9.4109 \text{ Å}, \) and \( \beta = 116.94^\circ , \) which are close to the experimental results of \( a = 8.5080 \text{ Å}, b = 8.5160 \text{ Å}, c = 9.3380 \text{ Å}, \) and \( \beta = 116.87^\circ . \)

3.1. Tritium Adsorption and Diffusion in the Perfect Li₃TaO₄ Crystal

First of all, the adsorption and diffusion of
tritium atoms in the perfect Li₃TaO₄ crystal are thoroughly studied. As we know, the diffusion of a tritium atom takes place between different stable and metastable sites, and thus, the adsorption of tritium in different sites should be investigated first. Preliminary tests show that the T atom will be adsorbed by the O atom to form a tritium–oxygen (T−O) bond regardless of the initial positions. Therefore, the tritium adsorptions on different types of O atoms are calculated and analyzed. Totally, four types of O atoms (types A–D) have been plotted in Figure 1.

Around each type of O atom, the tritium atom is placed at eight initial positions, which are 1.1 Å away from the O atom, and then the entire system is optimized by DFT calculations. The results show that the adsorption energy varies from 0.21 to 0.57 eV, with the difference in different types of O atoms less than 0.4 eV, and the length of the T−O bond is about 0.98 Å.

### Table 2. Lowest Energy Barrier for 15 Types of Tritium-Diffusion Pathways inside Each Type of Li Vacancy

| path | pathway | type I (eV) | type II (eV) | type III (eV) |
|------|---------|------------|-------------|--------------|
| path 1 | site 1–4 | 0.63       | 0.75        | 0.68         |
| path 2 | site 1–6 | 1.09       | 0.75        | 0.59         |
| path 3 | site 1–3 | 0.57       | 1.18        | 0.39         |
| path 4 | site 1–5 | 0.66       | 0.65        | 0.94         |
| path 5 | site 2–4 | 0.72       | 0.56        | 0.82         |
| path 6 | site 2–6 | 0.49       | 0.65        | 0.60         |
| path 7 | site 2–3 | 0.45       | 0.48        | 0.97         |
| path 8 | site 2–5 | 0.73       | 1.29        | 0.61         |
| path 9 | site 4–6 | 0.55       | 0.40        | 1.21         |
| path 10 | site 6–3 | 0.45       | 0.99        | 0.47         |
| path 11 | site 3–5 | 0.54       | 0.58        | 0.59         |
| path 12 | site 5–4 | 1.11       | 0.65        | 0.66         |
| path 13 | site 1–2 | 2.49       | 3.07        | 3.06         |
| path 14 | site 3–4 | 2.58       | 3.09        | 3.06         |
| path 15 | site 5–6 | 2.34       | 2.99        | 3.06         |

![Figure 2](image)

**Figure 2.** LDOS of tritium (T) and oxygen (O) atoms in the diffusion path 1 (a, b) and path 5 (c, d).

![Figure 3](image)

**Figure 3.** (a) Primitive cell of the Li₃TaO₄ crystal. (b) Defect model of the Li₃TaO₄ crystal with type II lithium vacancies. (c) Sketch map of the octahedron configuration of each type of Li vacancy.
Å, with the difference less than 0.01 Å. At the same time, each O atom has multiple metastable adsorption sites, with an energy difference of less than 0.3 eV. This fact implies that the T atom could migrate between different metastable adsorption sites on the same O atom at very low temperatures.

Based on the above results, the tritium-diffusion pathways in the perfect Li3TaO4 crystal are calculated. The energy barriers in the considered pathways are treated with the climbing image nudged elastic band (NEB) scheme. Considering the tritium diffusion between all of the four types of O atoms (types A–D), the T-diffusion pathways can be divided into 10 types, which are listed in Table 1. For instance, path 1 is the pathway A−A, which corresponds to the pathway from one oxygen atom of type A to another oxygen atom of the same type. For each type of diffusion pathway, a number of cases including pathways between different metastable sites have been calculated, and finally, the lowest diffusion energy barrier for each type of pathway is obtained and presented in Table 1. As it is shown, the highest energy barrier is 1.20 eV, which exists in path 1, and the lowest energy barrier is 0.34 eV in path 5.

Figure 5. Diffusion coefficient for the perfect and defect models of the Li3TaO4 crystal.
high when the path length is long and vice versa. When the diffusion path is longer, the distance of the T–O bond gets longer and the interaction is weakened, which may influence the distribution of the potential-energy surface and finally lead to the high diffusion-energy barrier.

To further verify this fact, we analyze the local density of states (LDOS) of T and O atoms in the longest path 1 and the shortest path 5, which has been plotted in Figure 2. The corresponding O atoms are at both ends of the diffusion paths 1 and 5, respectively. The LDOS in Figure 2a,b indicates that when tritium diffuses in the longer path 1, the T–O bond breaks, which results in the higher energy barrier. The peaks appearing near the Fermi level in Figure 2c,d imply that the T–O interaction is stronger during the tritium diffusion in path 5 than in path 1. Thus, we could conclude that the energy barriers for the different pathways are influenced by the pathway length, which is related to the T–O interaction during the diffusion.

It is worth noting that the diffusion pathway with a high energy barrier actually could be implemented by the combination of other paths with a lower energy barrier. This means that the tritium atom actually does not have to diffuse through the pathway with a high energy barrier to migrate in the crystal. For example, path 1 from A to A can be performed along the way of A–C–B–D–A, which corresponds to path 6–path 8–path 9–path 7, and the highest barrier in these diffusion pathways is 0.83 eV. Considering the combination of pathways, we conclude that the tritium could diffuse in the perfect Li3TaO4 crystal with a minimum energy barrier of 0.34 eV, which means that T could migrate easily in the Li3TaO4 crystals at low temperatures.

### 3.2. Tritium Adsorption and Diffusion inside the Li Vacancy of Li3TaO4

Lithium vacancies are considered as primary irradiation-induced defects in lithium-based breeder materials, as lithium atoms are constantly knocked out of their positions or consumed to generate tritium under irradiation. In the Li3TaO4 crystal plotted in Figure 3a, there are three different kinds of Li atoms, which correspond to three types of Li vacancies (types I–III). The labels of different colors listed on the right correspond to the different types of atoms, respectively. The adsorption and diffusion inside each type of Li vacancy are simulated and thoroughly analyzed in this section.

To ensure the reliability of the results, the formation energy of each Li vacancy in the 2 × 1 × 1 supercell and 2 × 2 × 2 supercell are calculated respectively. Comparing the results in the two supercells, the formation energy difference is less than 0.15 eV. For instance, the formation energy of the type I Li vacancy in the 2 × 1 × 1 supercell is 3.55 eV, while it is 3.41 eV in the 2 × 2 × 2 supercell. These results further validate the reliability of our theoretical model. On top of this, the obtained formation energies of three types of Li vacancies are 3.55, 3.40, and 3.40 eV, respectively.

Same as in the previous section, the adsorption properties of tritium in the vacancies are studied first. In each vacancy, the dangling bond of the O atoms generated by removing the Li atom will be the best adsorption sites for the T atom. Hence, there are six adsorption sites in each type of vacancy.

As shown in Figure 3b,c, each Li vacancy is actually an octahedron composed of six O atoms with dangling bonds. The obtained adsorption energies of T at six sites in each type of Li vacancy are very close to each other, which vary from −4.85 to −4.60 eV. At the same time, in all cases, the optimized T–O bond length is 0.98 Å, with differences of less than 0.01 Å, and all of the T–O bonds point toward the approximate center of the Li vacancy. This indicates the strong adsorption of the tritium atom in the vacancies. The results predict that the lithium vacancies in Li3TaO4 have similar tritium-trapping capabilities.

Next, we use NEB calculations to probe the tritium diffusion inside each type of Li vacancy of the Li3TaO4 crystal, respectively. The lowest energy barriers for all of the tritium-diffusion pathways inside each type of Li vacancy are listed in Table 2.

For instance, path 1 in Table 2 is related to the pathway from the adsorption site 1 to the adsorption site 4 in the Li vacancy as shown in Figure 3a. Path 9 inside a type II Li vacancy has been illustrated in Figure 3b, which corresponds to the tritium diffusion from site 4 to site 6. For each type of Li vacancy, 15 diffusion pathways have been calculated. Paths 1–12 called “edge paths” are pathways along the edge of the octahedral vacancy, while paths 13–15 called “diagonal paths” are along the diagonal direction of the octahedral vacancy. These 15 pathways encompass all cases when T diffuses inside the Li vacancy.

The energy barriers of the three diagonal paths (paths 13–15) in each type of vacancy are much higher than those of the edge paths. This fact means that tritium prefers to move along the edge of the octahedron when diffusing inside the vacancy. The energy barrier difference in different paths is probably related to the lengths of the paths. The mean pathway length of the edge paths is 1.85 Å, while the average diagonal pathway length is 2.5 Å. This fact is consistent with the results in the previous section.

Furthermore, it must be considered that a diffusion pathway with a high energy barrier could be achieved by combining diffusion paths with lower energy barriers. For example, the pathway of path 12 is from site 5 to site 4, and its corresponding energy barrier in the type I Li vacancy is 1.11 eV in Table 2. This pathway could be achieved by combining
path 8 (site 2–5) and path 5 (site 2–4), which reduces the energy barrier to 0.73 eV.

Generally, we could obtain that the minimum energy barrier of all of the diffusion paths inside each type of vacancy as 0.45, 0.40, and 0.39 eV, respectively. Therefore, it is found that the diffusion behavior of the T atom moving inside the Li vacancy is different from that in the crystal, namely, the T atom can move more easily in the crystal or inside the vacancies.

### 3.3. Tritium Hopping out of the Li Vacancy of Li3TaO4

Only the diffusion behavior of T in the perfect crystal and inside the Li vacancies does not fully describe the diffusion process of T in Li3TaO4. How a T atom jumps out of a Li vacancy is a fundamental problem, which will be discussed subsequently. In this section, we calculate the energy barrier of a T atom diffusing from the adsorption site inside the Li vacancy to the adsorption site outside the Li vacancy to understand how the tritium atom escapes from the vacancy.

Preliminary tests have shown that the tritium atom is always adsorbed to the oxygen atom after geometry optimization. We find that there are eight saturated O atoms close to the Li vacancy in the crystal, which are called “edge O atoms” and plotted as purple balls in Figure 4. The tritium adsorption energies at eight edge O atoms are from −4.22 to −3.99 eV, and the energy differences in three types of Li vacancies do not exceed 0.23 eV. After a careful comparison of the local density of states, it is found that these eight edge O atoms have the same properties as the saturated O atoms in the perfect Li3TaO4 crystal. Therefore, the process of T atom hopping out of the Li vacancy is actually the process in which the T atom diffuses from the O adsorption site with a dangling bond inside the vacancy to the adsorption site of the saturated edge O atoms close to the vacancy.

In Figure 4b, the structure formed around the Li vacancy is plotted, in which the eight purple edge O atoms form a quasi-cubic cage and the six black O atoms with dangling bonds are present at positions close to the face center of the cage. Each edge O atom has three nearest-neighboring O atoms with dangling bonds, namely three nearest-neighboring O atoms inside the Li vacancy. Therefore, there are 24 possible diffusion pathways for each Li vacancy. All of these possible diffusion pathways are calculated, and the related results are given in Table 3. Path 19 with a type II Li vacancy in Table 3 corresponds to the pathway from the edge O atom 7 to the adsorption site 1, which has been plotted in Figure 4a.

The results in Table 3 show that among the three types of Li vacancies, the minimum energy barriers for tritium jumping out the vacancy are 0.72, 0.70, and 0.51 eV, respectively. This indicates that the energy barrier that the T atom needs to jump out of the vacancy is a bit higher than the barrier for the T atom to diffuse in the crystal or inside the vacancy. It is easier for tritium to escape from the trap of a type III Li vacancy compared with other vacancies.

#### 3.4. Diffusion Coefficient

The diffusion coefficient is further investigated to reveal the tritium-diffusion behavior in the Li3TaO4 crystal. According to the previous study of the γ-LiAlO2 crystal, the diffusion coefficient D can be written as follows:

\[
D \approx \frac{l^2}{6} R_0 \gamma e^{-E_a/K_B T}
\]

where \(l\) is the migration distance, namely the length of the diffusion path; \(R_0\) is the attempt frequency; \(Z = 6\) is the coordination number; \(E_a\) is the activation energy barrier; \(K_B\) is the Boltzmann constant; and \(T\) is the temperature. According to the theory of Wert and Zener, \(R_0\) can be written as

\[
R_0 \approx \sqrt{\frac{2E_a}{m l^2}}
\]

and the diffusion coefficient can be written as

\[
D \approx l \frac{2E_a}{m} e^{-E_a/K_B T}
\]

To confirm the accuracy of this equation, the diffusion coefficients in the previous study\(^{23}\) have been calculated, and the results are consistent with it in the order of magnitude. Therefore, based on our calculated \(l\) and \(E_a\), the diffusion coefficient versus \(T\) for the perfect and defect models of the Li3TaO4 crystal are then obtained by eq 5, which have been illustrated in Figure 5.

The curve with solid black squares in Figure 5 is the result for tritium diffusing in the perfect crystal, the curve with red circles corresponds to the result for tritium diffusing inside the type III Li vacancy, and the curve with solid blue triangles is related to the result for tritium hopping out of the type III Li vacancy. The two vertical dashed lines mark the two corresponding temperatures, 300 and 600 K, respectively.

As shown in Figure 5, the tritium diffusion coefficient \(D\) at 300 K in the perfect crystal is much higher than those of the other two cases. However, as the temperature increases, the magnitude difference of the diffusion coefficient for the three curves is significantly reduced. The summary of tritium activation energy barriers, migration distances, and diffusion coefficients is presented in Table 4.

The detailed data in the above table have further presented that tritium prefers to diffuse in the type III Li vacancy because the corresponding diffusion coefficients are lower in contrast to the other two vacancies. This may due to the fact that tritium is easier to escape from the trap of the type III Li vacancy compared with the other vacancies in the previous section.

Besides, we compare our results with those of other lithium ceramic materials. In the latest theoretical study,
\(^{23,24}\) the smallest activation energy barrier inside the Li vacancy is 0.3 eV for Li2ZrO3 and 0.63 eV for \(γ\)-LiAlO2, while our result is 0.39 eV in a type II Li vacancy of Li3TaO4. The tritium diffusion coefficients at 600 K are approximately \(10^{-9}, 10^{-12}\), and \(10^{-10}\) m²/s in the above three types of crystals correspondingly.

In the previous experimental study, the observed order of tritium diffusion coefficients in different lithium ceramic materials was \(D (\text{Li}_2\text{ZrO}_3) \approx D (\text{Li}_2\text{SiO}_4) > D (\text{Li}_2\text{O}) > D (\text{Li}_2\text{ZrO}_3) > D (\text{Li}_2\text{SiO}_4) > D (\text{γ-LiAlO}_2).\)

Thus, from this point of view, we believe that Li3TaO4 could act as a potential tritium breeder, and the diffusion energy barrier of tritium in the Li3TaO4 crystal is not the major factor for preventing tritium release.

### 4. SUMMARY

In this work, the diffusion behavior of a tritium atom in the perfect and the defect Li3TaO4 crystals has been thoroughly investigated using density functional theory calculations. All of the diffusion pathways when tritium is diffusing in the perfect crystal, inside the three types of Li vacancies, and hopping out of the vacancies have been studied in detail. The obtained minimum energy barrier for tritium diffusion in the perfect crystal is 0.34 eV, while it is 0.39 eV for tritium diffusing inside the Li vacancies and 0.51 eV for tritium hopping out of the Li
vorages. By further investigation, we reveal that energy barriers for the different pathways are influenced by the pathway length, which is related to the T–O interaction during the diffusion.

Considering both the energy barrier and the pathway length, the tritium diffusion coefficients are finally calculated and analyzed. We find that it is relatively hard for tritium to escape from the Li vacancy at room temperature, but this situation will be greatly alleviated as the magnitude of the diffusion coefficient increases when the temperature increases. In contrast to the previous study of LiAlO2 crystals, our obtained diffusion coefficients are basically higher, which is beneficial to the tritium diffusion and release process. Our results could further help understand the experiments and provide support for the use of Li3TaO4 as breeder materials.

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Notes

The authors declare no competing financial interest.

Acknowledgments

This work was supported by the National Natural Science Foundation of China (No. 51871158), Shanxi Applied and Basic Research Program (No. 201801D121084), Doctors’ Initial Foundation of TYUST (No. 20192036), and the Fund for Shanxi Key Subjects Construction.

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