Inclusion and diffusion studies of D in fusion breeding blanket candidate materials

Master Thesis presented by

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Abstract

Deuterium-Tritium (D-T) reaction is the most practical fusion reaction on the way to harness fusion energy. As tritium presents trace quantities on Earth [1], tritium fuel is essential to be generated simultaneously with the D-T reaction in a commercial fusion power plant. Tritium can be obtained in the lithium contained breeding blanket as a transmutation product of nuclear reaction $^6\text{Li}(n, \alpha)^7\text{T}$. $\text{Li}_2\text{TiO}_3$ is considered to be one promising candidate solid tritium breeder material, due to its high lithium density, low activation, compatibility with structure materials and high chemical stability. The tritium generated in $\text{Li}_2\text{TiO}_3$ breeding blanket needs to be collected and recycled back to the fusion reaction. Therefore, the study of the diffusion characteristic of breeder material $\text{Li}_2\text{TiO}_3$ is necessary to determine tritium mobility and tritium extraction efficiency.

In order to study tritium release mechanism of $\text{Li}_2\text{TiO}_3$ breeding material in a fusion power plant environment, a fusion like neutron spectrum is essential while it is now not available in any laboratory. One alternative is using ion accelerator or implantor to get energetic hydrogenic (H,D,T) ions impacting on breeding material, to simulate the tritium distribution situation. Because of the radioactive property of tritium which will complicate processing procedure, another isotope of hydrogen Deuterium is actually used to be studied. The defect structure in $\text{Li}_2\text{TiO}_3$, due to reactor exposure to fusion generated particles and $\gamma$ ray irradiation, is achieved by energetic Ti ions. SRIM program is implemented to simulate the D ion or Ti ion distributions after bombardment, as well as the defects. X-ray diffraction technique helps to identify phase compositions. Transmission electron microscopy technique is used to observe the microstructures.

The SRIM simulations indicate that for a single energy D implantation and Ti irradiation, both the D ion and vacancy distributions have a peaked depth profile in the $\text{Li}_2\text{TiO}_3$ samples. XRD results imply that the surface area under 200 nm is modified by the implanted D ions, while after D implantation and Ti irradiation the crystal structure in the SRIM predicted area ranging from the depth of 200 nm to 600 nm is damaged. The TEM images and electron diffraction patterns further prove the modified surface and bulk crystalline structure in the Ti ion damaged area. Predicted by the SRIM simulation, the oxygen vacancy dominates the defects in $\text{Li}_2\text{TiO}_3$, which may work as an accumulation center to deuterium and contribute to the deuterium release process under thermal desorption treatment in the future.
Chapter 1

Introduction

1.1 Fusion energy on Earth

According to the United States census, the world population has now reached more than 7 billion and newborn birth rate every day is approximately 0.2 million [2], which means a great demand of energy resources. And with the development of new technology, electricity plays a more and more important role in everybody’s daily life. Nowadays, energy supply mainly comes from fossil fuels, nuclear power and renewable sources and the consumption percentage worldwide is shown in Fig. 1.1, but unfortunately all the energy resources have their pros and cons. Renewable sources such as solar energy, wind, geothermal, biomass, hydropower do not emit greenhouse gases but capturing these resources is expensive, and many are intermittent due to the uncontrollable factors such as the wind, the tides, which complicates implementing them on a large scale. Nuclear fission power now contributes about one tenth of the total electricity production but compared with the fossil fuels it is still quite small. The disposal of high radioactive nuclear fission waste still remains a big challenge because of their long period half life. Fossil fuels including oil, coal and natural gas provides more than 67 percent of the world total energy, however the total amount diminishes after consumption due to their limited deposit. Many products of fossil fuels combustion are air pollutants and harmful to the environment, for example, greenhouse gas carbon dioxide, nitrogen oxides, sulfur dioxide and heavy metals. Eventually, the degree to which depending on fossil fuels will have to lessen as the planet’s known supplies decrease, the difficulty and cost of tapping remaining reserves increases, and the effect of their continued use on earth grows more dire. As a result, a new clean, safe and environmentally friendly power source is urgently needed to supply increasing demands of the world’s energy.

Fusion is the process in which light atomic nuclei, with enough kinetic energy, collide with each other to combine together to form a heavier nuclei releasing tremendous amount of energy. Fusion reaction is much more clean compared with fission reaction because there is no long-term radioactive waste produced. There is low risk of uncontrollable security issues as the fusion
1.1 Fusion energy on Earth

Figure 1.1: World electricity production from all energy sources in 2012. [3]

conditions are strict, when the conditions are not satisfied the plasma cools down and the reaction stops. When compared with fossil fuels, the by-product of Deuterium-Tritium (D-T) fusion reaction shown in Fig. 1.2 is non-toxic, non-radioactive gas helium, which is harmless and clean to the environment. Moreover, a fusion reaction is more than four million times energetic than combustion of fossil fuels. While a 1000 MW coal fired power plant requires 2.7 million tons of coal per year, a fusion power plant of the kind envisioned will only need 250 kilos of fusion fuels, half in Deuterium and half in Tritium.

\[
^2D + ^3T \rightarrow ^4\alpha + ^1n + 17.6\text{ MeV} \quad (1.1)
\]

where \(D\) is deuterium, \(T\) is tritium, \(\alpha\) is \(^4\text{He}\) and \(n\) is neutron.

The most familiar and biggest fusion power plant near the Earth is the Sun. Every second in the Sun, 600 million tons of hydrogen are being converted into helium and at the same time release a large amount of heat and energy. This fusion reaction happens deep inside the core center of the Sun, in which zone pressures are million of times more than the surface of Earth, and the temperature reaches more than 15 million Kelvin [5]. In order to take advantage of fusion energy on Earth, there are several light paired elements to achieve fusion as shown in Fig. 1.3. The D-T reaction, shown in Equ. 1.1, has been identified as the most efficient reaction for fusion devices because
in the D-T reaction the highest cross section can be obtained with a lowest nuclei energy compared with the others. The resources of D-T reactants are not easily accessible on Earth. Deuterium has a natural abundance in Earth’s oceans of about one atom in 6420 atoms of hydrogen [6], in every litre of seawater, for example, there are 33 milligrams of deuterium. However, tritium is a fast-decaying radioactive isotope of hydrogen which exists trace quantities in nature. For a self-sustainable fusion reactor or power plant, the tritium need to be produced during the fusion reaction, in which neutrons escaping the plasma interact with the lithium contained in the blanket wall.

![Figure 1.3: Cross section of different fusion reactions. [7]](image)

### 1.2 Test Blanket Module systems in ITER

ITER (International Thermonuclear Experimental Reactor) is an international nuclear fusion research project, funded and run by seven member entities: the European Union, Russia, China, India, Japan, South Korea and the United States. The ITER project aims to prove the technological and scientific viability of harnessing fusion energy, and to collect the data necessary for designing and subsequent first electricity producing fusion power plant. The ITER tokamak will be nearly 30 meters tall and weigh 23000 tons, now being constructed at Cadarache in the south of France [4].

One important mission of ITER is to verify tritium breeding blankets concepts proposed by seven members. As mentioned above, fusion fuel tritium is terrestrial limited on Earth, estimated currently at 20 kilos [4]. Even though ITER will procure tritium fuel in its twenty years operational time, self breeding tritium is necessarily needed in the future commercial fusion power plant. Tritium can be obtained by fusion generated neutron colliding with lithium nuclide present in the breeding blankets in ITER. There will be six experimental Test Blanket Modules (TBM) installed in the equatorial ports. Two of
them will come from Europe, while China, India, Korea and Japan will contribute one each. A schematic drawing of two Test Blanket Modules (TBM) in one port of the ITER vacuum vessel wall is shown in Fig. 1.4. There are 18 equatorial ports in the ITER vacuum vessel, and three of them numbering 2, 16 and 18 will be assigned to the Test Blanket Modules. Each port will house two TBM concepts. Over the years, the ITER TBMs will be irradiated by neutrons generated in fusion reaction. After the blanket experiments completed, the TBMs will be delivered back to the manufacturing members for further analysis.

Figure 1.4: Two Test Blanket Modules (TBM) in one port of ITER vacuum vessel wall. [4]

There are three main objectives of ITER Tritium Breeding Blankets: production and extraction of tritium with breeding ration larger than 1.0, conversion of kinetic energy of neutrons into heat and shielding from neutron radiation. Based on these principles, six TBMs concepts are proposed by ITER parties as illustrated in Tab. 1.1. The major component of tritium breeding blanket is the tritium breeder in solid or liquid phase containing lithium, which can produce tritium when bombarded with energetic neutrons. In order to self-sustain tritium fuel in the future fusion power plants, the study of production and extraction under a fusion reactor operation state of all the six TBM concepts is quite essential. $Li_2TiO_3$ is thought to be one of the most promising breeder candidate materials, because it has advantages over many aspects. $Li_2TiO_3$ has high Li atom density, low activation, high chemical stability, compatibility with structure materials and good tritium release characteristic at low temperatures.
1.3 Crystal Structure of $\text{Li}_2\text{TiO}_3$

The tritium fuel is expected to be produced in the tritium breeding blanket by lithium transmutation. Since the heat evolved by the D-T fusion reaction will be absorbed by the blanket and transported to the coolant and the tritium generated in the TBM needs to be recycled back, crystal structure, thermal properties and tritium transport of the breeder material are important parameters for breeding blanket. Previous studies have found out that there are three different crystal structures of $\text{Li}_2\text{TiO}_3$: $\alpha$, $\beta$ and $\gamma$ [9]. $\alpha-\text{Li}_2\text{TiO}_3$ is a metastable phase and transforms into a monoclinic phase $\beta-\text{Li}_2\text{TiO}_3$ when temperature exceeds 300°C. When the temperature is higher than 1215°C, $\text{Li}_2\text{TiO}_3$ will transit from the $\beta$ phase to the high temperature $\gamma$ phase $\text{Li}_2\text{TiO}_3$, which is cubic and crystallises in the NaCl-type structure.

The temperature distribution of the tritium breeder blanket has been estimated to range between 300 and 900°C, taking into account the nuclear heating [10], so it is necessary to understand the crystal structure of the monoclinic $\text{Li}_2\text{TiO}_3$. In all of the experimental studies reported to date, sintered polycrystalline samples are used, well-characterized specimens are desirable to clarify the bulk nature of conductivity of $\text{Li}_2\text{TiO}_3$ and expect an anisotropic properties. The crystal structure of monoclinic $\text{Li}_2\text{TiO}_3$ was originally determined by Lang in 1954 [11], and subsequently refined using multiple film photographic single-crystal X-ray data [12]. More recently, the crystal structure was refined by Kataoka and Takahashi [13]. According to their report, $\beta-\text{Li}_2\text{TiO}_3$ has the monoclinic $\text{Li}_2\text{SnO}_3$ type structure as is shown in Fig. 1.5. The structure

<table>
<thead>
<tr>
<th>Concept</th>
<th>Acronym</th>
<th>Materials</th>
<th>Proposing Parties</th>
</tr>
</thead>
<tbody>
<tr>
<td>Helium-Cooled Ceramic Breeder</td>
<td>HCCB/HCPB</td>
<td>FMS structures</td>
<td>EU,CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Be multiplier}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Li}_2\text{TiO}_3$, $\text{Li}_2\text{SiO}_4$ or $\text{Li}_2\text{O}$</td>
<td></td>
</tr>
<tr>
<td>Water-Cooled Ceramic Breeder</td>
<td>WCCB</td>
<td>FMS structures</td>
<td>JA</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Be multiplier}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>ceramic breeder $\text{Li}_2\text{TiO}_3$</td>
<td></td>
</tr>
<tr>
<td>Helium-Cooled Lithium-Lead</td>
<td>HCLL</td>
<td>FMS structures</td>
<td>EU,CH</td>
</tr>
<tr>
<td></td>
<td></td>
<td>liquid Pb-16Li</td>
<td></td>
</tr>
<tr>
<td>Lead-Lithium cooled Ceramic Breeder</td>
<td>LLCB</td>
<td>RAFM structures</td>
<td>IN</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Pb-Li and Li}_2\text{TiO}_3$</td>
<td></td>
</tr>
<tr>
<td>Helium Cooled Ceramic Reflector</td>
<td>HCCR</td>
<td>RAFM structures</td>
<td>KO</td>
</tr>
<tr>
<td></td>
<td></td>
<td>$\text{Be multiplier}$</td>
<td></td>
</tr>
<tr>
<td></td>
<td></td>
<td>Lithium ceramics</td>
<td></td>
</tr>
</tbody>
</table>

Table 1.1: Blanket concepts proposed by ITER parties for testing. [8]
1.3 Crystal Structure of $\text{Li}_2\text{TiO}_3$

is an ordered rock-salt super-structure with cationic (1 1 1) planes alternately occupied by layers of Li and (LiTi$_2$). Its unit cell has twenty-four atoms with lattice parameters displayed in Tab. 1.2 and unit cell definition is illustrated in Fig. 1.6.

![Figure 1.5: Crystal structure of $\text{Li}_2\text{TiO}_3$: medium grey, medium red and large blue balls correspond to Li, Ti, and O atoms, respectively.][13]

<table>
<thead>
<tr>
<th>Lattice parameters</th>
<th>a</th>
<th>b</th>
<th>c</th>
<th>$\alpha$</th>
<th>$\beta$</th>
<th>$\gamma$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\beta - \text{Li}_2\text{TiO}_3$</td>
<td>5.0622Å</td>
<td>8.7712Å</td>
<td>9.7487Å</td>
<td>90°</td>
<td>100.01°</td>
<td>90°</td>
</tr>
</tbody>
</table>

Table 1.2: Lattice parameters of $\beta - \text{Li}_2\text{TiO}_3$.[14]

![Figure 1.6: Unit cell definition using parallelopiped with lengths $a, b, c$ and angles between the sides given by $\alpha, \beta, \gamma$.][16]
Chapter 2

Objective

Lithium metatitanate ($Li_2TiO_3$) is one of the most attractive candidates as a solid breeder blanket in D-T fusion reactors. The use of this material presents several advantages: potentially high tritium generation and fast tritium release, low chemical reactivity, low thermal conductivity, and good compatibility with other materials at high temperature. The desired nuclear reaction taking place in this solid breeder ceramic is

$$^6Li + n \rightarrow T + \alpha + 4.8 \text{ MeV}$$

(2.1)

Where $n$ is a neutron, $T$ is tritium and alpha is a $^4\text{He}$ particle.

Because tritium fuel is generated in the Tritium Blanket Module (TBM) and then must be collected and recycled into the main reactor chamber, the desorption of the retained tritium at the operational temperature becomes an important parameter to study and control in order to achieve a self-sustainable operation. The tritium release characteristics consist of a complex combination of gas diffusion stages inside the solid. Considering that this ceramics will produce high concentration of gaseous transmutation products when exposed to high-energy neutrons, there are considerable interests in studying $T$ diffusion for the fundamental understanding of the light ion behavior in breeder blanket materials under reactor conditions. Because the high $T$ activity, its volatile and long decay time lead to complex and rigid safety procedures. In order to analysis $T$ behavior, reactor irradiation tests are simulated by ion implantation of other light species such as D which is easier to handle with and an isotope of $T$.

In an attempt to understand the mechanisms for the light ion transport in a fusion nuclear environment, three different sets of D inclusion and damage irradiation experiments on fusion candidate Lithium Metatitanate ($Li_2TiO_3$) are proposed: (1) a peaked Ti irradiation damaged area starting from the surface, after which is a peaked D implanted area; (2) peaked Ti irradiation damage and D implantation areas coincide with each other; (3) uniform damage and D distribution start from the surface to a depth around 8000 Å. The three implantation and irradiation experiments are designed in order to simulate the situation inside the tritium blanket module after the transmutation process,
especially the third uniform case, which is thought to be the most realistic condition.

Due to the irradiation impact on the breeding material and light ion implantation, it is believed that it would have some effects on the crystalline structure or morphological properties of lithium metatitanate, so several techniques are needed to analyse and identify those modifications. X-ray diffraction is a powerful technique to investigate and quantify the crystalline nature of materials by measuring the diffraction of x-rays from planes of atoms within the material. It will be used to characterize the structures of as-prepared and after implanted samples to conclude if there is any and what kind of crystalline structure modifications due to the irradiation and implantation. The Transmission electron microscope (TEM) is an analytical tool allowing visualization and analysis of specimen in the realm of microspace (1 micron = 10^{-6} m) to nanospace (1 nm = 10^{-9} m). It uses a beam of electrons penetrating the specimen with an electron illuminated material or a camera to obtain an image. With the transmission electron microscopy technique, it is capable of detailed micro-structural examination through high-resolution and high magnification imaging. And the electron diffraction pattern can benefit the investigation of the crystal structure before and after the irradiation and implantation in $Li_2TiO_3$. 


Chapter 3

SRIM simulation

3.1 Non-coincident peaked Ti irradiation and D implantation

SRIM (the Stopping and Range of Ions in Matter) software is implemented to simulate the collision events and ion distributions when the target material is bombarded by energetic ions. The screen shots of the two SRIM interfaces are shown in Fig. 3.1: Fig. 3.1a illustrates the ion stopping and range tables, from which one can quickly obtain basic information of a specific implantation including ion projected range, longitudinal straggling and lateral straggling; and Fig. 3.1b shows the TRIM calculation window for inputs. In the simulation, the target material is Lithium Metatitanate ($\text{Li}_2\text{TiO}_3$), and the target density used here is 2.7 g/cm$^3$ according to Ref. [15] rather than the theoretical one.

![Screen shots of SRIM interfaces](image)

(a) stopping and range tables  
(b) TRIM calculation

Figure 3.1: Screen shots of SRIM interfaces

The first simulation is chosen to have both a peaked titanium (Ti) irradiation damage and a peaked deuterium (D) implantation distribution in the target material. The chosen ion types and energies are shown in Tab. 3.1 including the projected range from the SRIM range calculation table.
3.1 Non-coincident peaked Ti irradiation and D implantation

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Ion energy (eV)</th>
<th>Projected range (Å) [from SRIM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>D⁺</td>
<td>70</td>
<td>7504</td>
</tr>
<tr>
<td>Ti⁺</td>
<td>600</td>
<td>5231</td>
</tr>
</tbody>
</table>

Table 3.1: Selected ions and energies in peaked Ti irradiation and D implantation.

The collision events and atom distributions in the target material after the 600 keV Ti⁺ irradiation are illustrated in Fig. 3.2 and Fig. 3.3. As is shown in Fig. 3.2, the maximum vacancies of the three Li, O and Ti atoms appear at the same target depth. Moreover, oxygen vacancy dominates the main contribution to the total vacancies compared to Lithium (Li) and Titanium (Ti).

![Figure 3.2: Collision events in Li₂TiO₃ for a 600 keV Ti⁺ irradiation in SRIM simulation.](image)

Final recoil atom and incident Ti ion distributions are shown in Fig. 3.3. All the three target atoms have the maximum distribution at the same target depth at about 4000 Å and oxygen atom is also the dominant one compared with Li and Ti atoms, in Fig. 3.3a. The Bragg peak of incident Ti ion appears at around 5500 Å in Fig. 3.3b, which is consistent with Tab. 3.1. Moreover, when comparing the Ti ion and the target recoil distribution, one can easily find out that the magnitude of Ti ion is three orders less than the magnitude of Ti target recoil atom, so the contribution from the incident Ti ion is negligible in the total Ti atom distribution.

In a SRIM simulation for a 70 keV D⁺ bombarding on Lithium Metatitanate, the outcomes for collision events and atom distributions are illustrated in Fig. 3.4. Compared with the vacancy distribution shown in Fig. 3.2, the damage done by a 70 keV D⁺ ion is at least two orders of magnitude less than a 600 keV Ti⁺ ion. Also, the target atom distribution is negligible compared to the one in a 600 keV Ti⁺ ion irradiation. So when plotting the total damage distribution in the target material under both irradiation and implantation,
3.1 Non-coincident peaked Ti irradiation and D implantation

Figure 3.3: Atom distributions in \( \text{Li}_2\text{TiO}_3 \) for a 600 keV \( \text{Ti}^+ \) irradiation in SRIM simulation

Figure 3.4: Outcomes in SRIM simulation when \( \text{Li}_2\text{TiO}_3 \) is implanted with a 70 keV \( \text{D}^+ \) ion.

damage from \( \text{Ti}^+ \) is the only one taken into consideration.

Fig. 3.5 shows the vacancies and deuterium atom distributions when the target material is both irradiated and implanted by ions specified in Tab. 3.1. Except for the total vacancies, oxygen vacancies is also illustrated because in Ref. [16], it mentioned that oxygen vacancies seem to be a very important factor in the diffusion of tritium in the ceramic breeding blanket. As is shown in Fig. 3.5, three different regions can be observed: a damaged area from surface to around 5000 Å, a deuterium concentrated area ranging from 6000 Å to 10000 Å, and lastly the totally un-damaged and un-implanted bulk area.
3.2 Coincident peaked Ti irradiation and D implantation

Another situation in which the peaks of vacancies and deuterium distribution coincided with each other is also simulated. The chosen ion types and energies are shown in Tab. 3.2. Compared to the previous case, the deuterium distribution is the same, while the Ti ion energy is increased to obtain the damage further into the target material. Fig. 3.6 shows a good agreement with the two sets of peaks from vacancy and deuterium ion distributions.

<table>
<thead>
<tr>
<th>Ion type</th>
<th>Ion energy (eV)</th>
<th>Projected range (Å) [from SRIM]</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D^+$</td>
<td>70</td>
<td>7504</td>
</tr>
<tr>
<td>$Ti^+$</td>
<td>1000</td>
<td>8507</td>
</tr>
</tbody>
</table>

Table 3.2: Selected ions and energies in coincident peaked Ti irradiation and D implantation.

3.3 Uniform Ti irradiation and D implantation

Compared to the peaked case, in a more realistic operation with tritium breeding blanket, a uniform distribution of damage by energetic ions and electromagnetic waves will occur, and a uniform deuterium is generated from the nuclear reactions $^6Li$ (n, α)T or $^7Li$ (n, n α) T when the ceramics are irradiated with neutrons. So the next simulation is done with an attempt to achieve a nearly uniform distribution of both material damage and impurity.
3.3 Uniform Ti irradiation and D implantation

Figure 3.6: Vacancies and D distribution in $\text{Li}_2\text{TiO}_3$ after a 1000 keV $\text{Ti}^+$ irradiation and a 70 keV $\text{D}^+$ implantation in SRIM simulation. Concentration. $\text{Ti}^+$ ion energies are chosen in the sequence way as illustrated in Tab. 3.3, which increases energies with bigger intervals at the beginning and smaller intervals after the energy 1000 keV.

<table>
<thead>
<tr>
<th>$\text{Ti}^+$ ion energy (keV)</th>
<th>100</th>
<th>300</th>
<th>500</th>
<th>700</th>
<th>900</th>
<th>1000</th>
<th>110</th>
<th>1200</th>
<th>1300</th>
<th>1400</th>
</tr>
</thead>
<tbody>
<tr>
<td>Projected range (Å)</td>
<td>872</td>
<td>2602</td>
<td>4362</td>
<td>6082</td>
<td>7722</td>
<td>8507</td>
<td>9267</td>
<td>10000</td>
<td>10700</td>
<td>11400</td>
</tr>
</tbody>
</table>

Table 3.3: Selected Ti energies in uniform irradiation.

This set of energies is chosen in this way only to obtain a uniform vacancy distribution as shown in Fig. 3.7. It can be observed from the individual vacancy distributions of different ion energies that the vacancies are generated starting from the surface for all the energies, which means that there is an accumulation effect in the near-surface area. So it is necessary to implement different energy intervals in the near and far target area to achieve a uniform vacancy distribution. The top blue line in Fig. 3.7 shows the total vacancy distribution from all the chosen $\text{Ti}^+$ energies, and a uniform vacancy distribution can be seen ranging from around 500 Å to 8000 Å. One may notice that there is a sudden decrease in the total vacancy distribution at around 1500 Å, it can be compensated by a lower fluence of 200 keV $\text{Ti}^+$ ion irradiation when implementing experiments.

In order to obtain a uniform deuterium distribution in the target material, a set of implanted ion energies is chosen as shown in Tab. 3.4. Different with the case in $\text{Ti}^+$ irradiation in Fig. 3.7, the deuterium distribution for a single energy is a more sharp peaked one, which means the deuterium atom concentrates in the near area of the Bragg peak. The uniform distributions of damage and deuterium atoms are shown in Fig. 3.8. It can be seen that the SRIM simulation gives a uniform distribution in the range from around 500 Å
3.3 Uniform Ti irradiation and D implantation

Figure 3.7: Total and separate vacancy distributions for different $Ti^+$ ion energies.

to 8000 Å for both damage and deuterium atom. However, there is a decrease at around 3000 Å, which can be compensated by a lower fluence of 25 keV $D^+$ ion.

<table>
<thead>
<tr>
<th>$D^+$ ion energy (keV)</th>
<th>5</th>
<th>10</th>
<th>20</th>
<th>30</th>
<th>35</th>
<th>50</th>
<th>60</th>
<th>70</th>
<th>80</th>
</tr>
</thead>
<tbody>
<tr>
<td>Projected range (Å)</td>
<td>873</td>
<td>1645</td>
<td>2960</td>
<td>4056</td>
<td>4551</td>
<td>5903</td>
<td>6727</td>
<td>7512</td>
<td>8267</td>
</tr>
</tbody>
</table>

Table 3.4: Selected D energies in uniform implantation.

Figure 3.8: Uniform vacancy and D distribution in $Li_2TiO_3$ in SRIM simulation.
Chapter 4

Experimental details

$Li_2TiO_3$ ceramics pellets were fabricated in LNF-CIEMAT laboratories (Spain) starting from a commercial powder (Alfa Aesar, 99.9% purity), isostatically pressed at 230 MPa, sintered in air at 1350°C for 4h and then cut into 15 mm diameters discs of 200 um thickness.

The non-coincident peaked implantation and irradiation experiment has been performed in UCM, while the other two simulated cases are suggested to be performed in the future in the facilities with details explained below.

4.1 Non-coincident Peaked implantation and irradiation

Prior to the D implantation, the as-received $Li_2TiO_3$ sample was irradiated in the UCM (Universidad Complutense de Madrid, Spain) with a 150 keV $Ti^{4+}$ beam and a fluence of $10^{15}$ ions/cm$^2$ to a depth of 500 nm. It is necessary to mention that in SRIM simulation the irradiation is done with a 600 keV $Ti^+$ beam while here a 150 keV $Ti^{4+}$ is used. This is because the SRIM software is not able to distinguish between different ion states, indicating that a 600 keV $Ti^+$ beam and a 600 keV $Ti^{4+}$ beam will have the identical damage effect in the SRIM outcome. So in the experiment, rather than use $Ti^+$ ions accelerated by a 600 kV voltage which will generate 600 keV $Ti^+$ ions, a lower accelerating voltage applied on a higher ion state is implemented: 600 keV $Ti^{4+}$ ions can be obtained when $Ti^{4+}$ ions are accelerated by a 150 kV voltage. Then Deuterium ions ($D^+_2$) were implanted in the UCM (Madrid, Spain) facility with a 70 keV beam to a total fluence of $10^{17}$ at./cm$^2$ into a depth of 750 nm. Structural characterization of as-received, irradiated and implanted samples was carried out by X-ray diffraction (XRD) using a Philips X-PERT-MPD diffractometer with a Cu kalpha-radiation source. The microstructure was observed by transmission electron microscope (TEM) in URJC (Universidad Rey Juan Carlos, Madrid, Spain).
4.2 Coincident peaked case

Different from the previous experiment, a higher $Ti^{+}$ energy will be implemented in order to obtain an coincident area in which both damage and D distribution peak are contained. Moreover, instead of bombarding the target material with $D_{2}^{+}$ ions after $Ti^{+}$ ions, the irradiation and implantation will take place at the same time, because it is believed that a simultaneous bombarding with both $Ti^{+}$ and $D_{2}^{+}$ ions will be quite different with the sequential bombardment regarding to the damage and D distribution in the target material. The $D_{2}^{+}$ ions will be implanted in TIARA (Takasaki Ion Accelerators for Advanced Radiation Applications, Japan) by a 70 keV ion beam at a fluence of $10^{17}$ at/cm$^{2}$ at normal incidence to a depth of 750 nm (SRIM calculations), and at the same time the target material is irradiated by a $Ti^{4+}$ ion beam with an energy of 1000 keV and a fluence of $10^{15}$ ions/cm$^{2}$ to a depth of 8500 $\alpha$.

4.3 Uniform case

The ion-irradiation research facility TIARA consists of four accelerators, an AVF cyclotron, a 3-MV tandem accelerator, a 3-MV single ended accelerator and an ion implanter, which makes it qualified for higher energies irradiation and implantation. In order to achieve a uniform damaged and implanted area, a series of energies are necessary based on SRIM simulations. So the Ti irradiations will be carried out in TIARA (Takasaki, Japan) with a sequence of various energies: 100, 300, 500, 700, 900, 1100, 1200, 1300, 1400 keV, and each of them has a total fluence of $10^{14}$ at/cm$^{2}$. What’s more, another special energy level will need to be added to compensate the vacancy intensity drop around 200 nm shown in Fig. 3.8, that is a 200 keV $Ti^{4+}$ ion beam with a total fluence of $10^{13}$ at/cm$^{2}$. Then the target material will be implanted with $D_{2}^{+}$ ions with a sequence of energies: 5, 10, 20, 30, 35, 50, 60, 70, 80 with a fluence of $10^{16}$ at/cm$^{2}$ each, and a special energy level of 25 keV $D_{2}^{+}$ ion beam with a total fluence of $10^{15}$ at/cm$^{2}$. After the D implantation and Ti irradiation, structural characterization of implanted and irradiated sample will be carried out by X-ray diffraction (XRD). The microstructure will be observed by the transmission electron spectroscopy, along with electron diffraction to study the nano crystal structure in D implanted and Ti irradiated $Li_{2}TiO_{3}$. The distribution of D atom in D implanted and Ti irradiated $Li_{2}TiO_{3}$ sample can be obtained by the use of nuclear reaction analysis (NRA) technique. The thermal desorption spectrum analysis will be implemented along with the electron spin resonance (ESR) method to study the correlation between deuterium release behavior and annihilation of irradiated induced defects. Besides, the study of relationship between deuterium release rate with purge gas species, sweep gas flow rate and hydrogen content in the purge gas is need to further analyze the deuterium release mechanism.
Chapter 5

Results and discussion

5.1 X-ray diffraction

5.1.1 Basic physical principle of X-ray crystallography

X-ray crystallography is a tool used for identifying the atomic and molecular structure of a crystal, in which the periodic crystalline atoms cause a beam of incident x-rays to diffract into many specific directions. This branch of science based on x-ray diffraction is the crystal structure analysis of simple organic compounds, minerals, organic molecules, and biological macromolecules. The translation periodicity in a crystal lattice is about the same order of magnitude as the wavelength of X-rays, so the x ray can be diffracted in a periodic crystal structure, which is similar to the case that a visible light can be diffracted in a grating grid. Moreover, the X-ray diffraction in a crystal could be treated by adding one more diffraction equation to the two-dimensional diffraction of a cross-grid pattern. X-ray diffraction in a crystal could be treated as reflection from parallel lattice planes as shown in Fig. 5.1.

![X-ray diffraction schematic](image)

Figure 5.1: The schematic illustration of x-ray diffracted by parallel lattice planes. [17]

Crystals are regular arrays of atoms, and X-rays are electromagnetic radiation. When the x ray encounters the charged particles, in this case the positive nucleus and negative electrons orbiting around it, the electric field component
of the incident electromagnetic wave accelerates the charged particles, causing them to emit radiation at the same frequency as the incident wave, so an X-ray striking an atom produces secondary spherical waves emanating from the atom. Atoms in crystal structures scatter x-rays, primarily through the atom’s electrons, and a regular array of atoms produces a regular array of spherical waves. Although these spherical waves cancel one another out in most directions through destructive interference, they add constructively in a few specific directions, determined by Bragg’s law Equ. 5.1.

\[ 2d \sin \theta = n \lambda \]  

where \( d \) is the spacing between diffracting planes, \( \theta \) is the incident angle, \( n \) is an interger, and \( \lambda \) is the wavelength of the x ray beam.

As is shown in Fig. 5.1, the incident x-ray beam coming from the upper left interacts with the electrons in the atom then re-radiate from the atom located in the crystal structure. And also the secondary wave can be regarded as a ”reflected” wave, in which the reflected angle is the same as the incident one at the same frequency. If the atoms are arranged symmetrically with a separation distance \( d \), the ”reflected” waves will be added constructively only in directions where their path-length difference \( 2d \sin \theta \) equals an integer multiple of the wavelength \( \lambda \). In that case, part of the incoming beam is deflected by an angle \( 2\theta \), producing a diffraction pattern.

### 5.1.2 X-ray diffractometer geometries

X-ray diffractometer consists of an X-ray source, a sample stage, a detector and a way to vary angle \( \theta \) as is illustrated in Fig. 5.2. Bragg Brentano geometry is the conventional powder diffraction geometry as shown in Fig. 5.2, in which the detector, the X-ray source tube and the sample are moved in such a way to guarantee the detector is always at \( 2\theta \) and the sample surface is always at \( \theta \) to the incident X-ray beam. For example, the tube is fixed while the sample rotates at \( \theta^\circ /\text{min} \) and the detector rotates at \( 2\theta^\circ /\text{min} \), or in another way, the sample is fixed, and meanwhile the tube rotates at a rate of \( -\theta^\circ /\text{min} \) and the detector rotates at a rate of \( \theta^\circ /\text{min} \). As the x ray penetrates into the studied material, the depth of analysis varies during the symmetrical sweeping \( \theta/2\theta \). More precisely, the x ray goes further into the sample as \( \theta \) increases according to Equ. 5.2.

\[ Z = L \times \sin(\theta) \]  

where \( Z \) is the vertical analysis depth, \( L \) is the penetrating length of an X-ray beam with a specific energy in a material which should be identical when both the target and the beam characteristics are fixed, and \( \theta \) is the incident angle.

So when the incident angle is closer to the plane normal, there is an intense signal from the substrate and a weak signal from the surface. Therefore, when studying the characterization of thin films, the conventional symmetrical
Bragg Brentano configuration is not suitable. In these cases, it is more convenient to implement the technique of X-ray diffraction at grazing incidence named Grazing Incidence Angle X-ray (GIAXRD) to minimize the contribution related to the substrate, which is shown in Fig. 5.3. In this geometry, the incidence angle ($\alpha$) is fixed at a small angle which exceeds the critical angle of total reflection, typically around 1° and 3°, while the angle between the incident beam and the diffracted beam varies, moving only the detector arm. Thus, the incident beam goes a long way in the surface area of interest which reduces the signal from the substrate due to the small incident angle $\alpha$. Moreover, the depth of analysis $Z$ will not vary with the sweeping angle $\theta$, in this case only depending on the identical incident angle $\alpha$. By using the GIAXRD, the analysis depth can be controlled by fixing the incident angle, and in the meantime focusing on the interested top-most surface of the sample.
5.1 X-ray diffraction

Powder diffraction is more aptly named polycrystalline diffraction, in which samples can be powder, sintered pellets, coatings on substrates, engine blocks and so on. A polycrystalline sample should contain thousands of crystallites in all different directions, therefore, all possible diffraction peaks should be observed. If the crystallites are randomly oriented and there are enough of them, they will produce a continuous Debye cone shown in Fig. 5.4. In a linear diffraction pattern, the detector scans through an arc that intersects each Debye cone at a single point, thus giving the appearance of a discrete diffraction peak.

![Debye-Scherrer rings in powder X-ray diffraction.](image)

5.1.4 XRD results

According to the sample producing processes elaborated in Chapter 4, the experimentally studied sample, the non-coincident peaked irradiated and implanted \( \text{Li}_2\text{TiO}_3 \), was fabricated by high temperature sintering process as described in Chapter 4. In the non-coincident peaked case, the concentrated depth of implanted \( D \) ions and the damaged area of irradiated \( Ti \) ions are limited in the top surface below 1200 nm, which means the topmost surface of the sample is the zone of interest. Therefore, conventional X-ray diffractometer geometry is not suitable, the grazing incidence X-ray diffraction (GIXRD) was then being implemented on the non-coincident peaked case sample.

As mentioned above, X-ray diffraction is a very practical technique to determine the phase composition of a sample. The diffraction pattern for every phase is unique as a fingerprint and crystalline phases with the same chemical composition can have drastically different diffraction patterns. Normally, the outcome of XRD is a signal presented in a two dimensional figure which is the absolute intensity versus the angle between the incident beam and the observation position \( \theta \). The absolute intensity, which is the number of X rays observed in a given peak, can vary due to instrumental and experimental parameters, hence rather than comparing the absolute value of X-ray intensity, the relative intensity comparison is more useful and reliable. The relative intensities are obtained by dividing the absolute intensity of every peak by the...
absolute intensity of the most intense peak, and then converting to a percentage, thus the most intense peak of a phase is called the "100%" peak. It is more practical to use the relative intensity to analyze the XRD patterns. Using the position 2θ and relative intensity of a series of peaks to match experimental data to the reference patterns in the databases such as Powder Diffraction File (PDF), one is able to determine the phase compositions of a studied sample with the help of some useful programs such as JADE. When referring to a XRD database, the diffraction peak whose absolute intensity is the highest will have 100% relative intensity in the I column.

The non-implanted and non-irradiated $Li_2TiO_3$ is named the as-received sample. After the original $Li_2TiO_3$ powder was sintered and cut into pellets, this as-received sample was examined by the GIXRD at the angles ranging from 0.1° to 1.3°, with an interval of 0.2°. At the same time, the x ray penetrating depths corresponding with different grazing incident angles are both illustrated in Tab. 5.1. As can be seen from Tab. 5.1, the bigger the incident angle is, the deeper the x-ray goes through the studied sample, which is consistent with the relationship shown in Equ. 5.2. To be more clear about the different observed depths, a schematic diagram illustrating the XRD beam penetrating depths and D implantation peak area is drawn in Fig. 5.5.

<table>
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<tr>
<th>XRD pattern numbering</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
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<tbody>
<tr>
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<td>0.3</td>
<td>0.5</td>
<td>0.7</td>
<td>0.9</td>
<td>1.1</td>
<td>1.3</td>
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<tr>
<td>Depth(nm)</td>
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<td>390</td>
<td>650</td>
<td>910</td>
<td>1170</td>
<td>1430</td>
<td>1670</td>
</tr>
</tbody>
</table>

Table 5.1: X ray ranges corresponding with different grazing incident angles. [21]

![Figure 5.5](image)

Figure 5.5: Schematic diagram of XRD beam depths suggested for the damaged and implanted sample based on SRIM simulation.

The grazing incidence angle X-ray diffraction pattern of the as-received $Li_2TiO_3$ sample is shown in Fig. 5.6. Instead of all the XRD patterns, four were chosen to be illustrated, which are incidence angles at 0.1°, 0.5°, 0.7° and
Moreover, in order to better compare the four different patterns, the four lines were aligned in a column with increasing incidence angle from down to top and each one of them shifted a little bit to the right with respect to the previous line. The inclined black straight line intersecting the four patterns indicates that the intersected points share the same position $2\theta$, which the four intersected positions are located at $20^\circ$, $40^\circ$, $60^\circ$ and $80^\circ$ in Fig. 5.6.

When analyzing the experimental XRD patterns, the highest peak is the first one to be considered, in this case, they are the peaks around $43^\circ$ for all the four patterns, and the second and third highest peaked near $18^\circ$ and $63^\circ$, respectively. Comparing the three highest peaks with the database, the as-received sample was determined to be the monoclinic $Li_2TiO_3$. To be more clear, related plane information from the database is illustrated in Tab. 5.2 and also Miller Indices of lattice planes were labeled with their corresponded peaks in Fig. 5.6. Even though these four XRD patterns belong to the non implanted and non irradiated sintered $Li_2TiO_3$ samples, they present slight discrepancies between each other. The XRD pattern at incidence angle $0.1^\circ$ behaves differently with the pattern at incidence angle $1.3^\circ$. The intensity of the peak representing the family of planes $(312,-206,-331)$ is much smaller compared to the one representing the $(-133)$ family of planes, and there is a trend that the further the X-rays penetrate into the sample, the similar the XRD pattern is to the previous one; for example, the pattern at incidence angle $0.7^\circ$ looks like the one at incidence angle $1.3^\circ$ except for some small differences. The reason for this difference may result from the sample preparation procedure. During the sintering process, due to some reason the crystal alignment in the near surface region has a preferred direction, but the bulk area has a homogeneous crystal direction distribution. As a result, the X-ray signal from the $(-133)$ family of planes is stronger than the others as the $0.1^\circ$ XRD pattern shown in Fig. 5.6. When the incidence angle goes beyond a certain angle, the bulk signal overcomes the surface signal significantly, the XRD patterns are alike just as the patterns at incidence angles $0.7^\circ$ and $1.3^\circ$.

In summary, the XRD patterns of the non implanted and non irradiated as-received sample are alike beyond an incidence angle at $0.7^\circ$, confirming that the bulk area of the sample presents the same crystalline pattern as expected. However, the crystalline pattern at surface is characteristic and different in XRD relative intensity with that of the bulk. Answer should be found in crystal modification due to the mechanical processes owning or performed to the surface, i.e. cutting, polishing, local different temperatures.
### 5.1 X-ray diffraction

<table>
<thead>
<tr>
<th>h</th>
<th>k</th>
<th>l</th>
<th>d [Å]</th>
<th>2Theta [deg]</th>
<th>I [%]</th>
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<td>1.16105</td>
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</tr>
</tbody>
</table>

Table 5.2: Related XRD peak information from monoclinic \(Li_2TiO_3\) PDF card. [22]
5.1 X-ray diffraction

Figure 5.6: X-ray diffraction patterns of as-received \( Li_2TiO_3 \) sample. [21]

Figure 5.7: X-ray diffraction patterns of D implanted \( Li_2TiO_3 \) sample. [21]
5.1 X-ray diffraction

Figure 5.8: X-ray diffraction patterns of Ti irradiated and D implanted $Li_2TiO_3$ sample. [21]

After the D implantation process, the sample was examined again by the GIXRD and the result is shown in Fig. 5.7. According to the SRIM simulation result, the main D implanted area is concentrated near the depth of 750 nm, which focuses on the XRD patterns at 0.5° and 0.7° with 650 nm and 910 nm penetrating depths respectively. Compare them with the ones in the as-received sample shown in Fig. 5.6. The relative intensity between the (-133) peak and the (002) peak almost remains the same after the D implantation process, which implies the crystalline structures does not change because of the implanted D. The amount of vacancies created by the D implantation are quite small according to Fig. 3.4a, so it should not modify the crystal structure, which is consistent with the non changed XRD patterns at angles 0.5° and 0.7°.

However, the XRD pattern at angle 0.1° changes after the D implantation. The relative intensity between the (-133) plane and (002) plane decreases significantly, which indicates that the (-133) plane from the surface to the depth of 130 nm is somehow modified by the implanted D ions and resulting in the decrease of the diffracted x ray by the (-133) family of crystal planes. Moreover, the XRD pattern with D implanted at 1.3° is slightly different in the two samples. The (-133) peak intensity overcomes (002) peak in the D implanted sample, while it is the opposite situation in the as-received sample. At the incidence angle 1.3°, the x ray beam will penetrate into the depth of 1670 nm, so most of the diffracted x ray signal comes from the bulk zone of the D implanted
sample. Because of the nonuniform distributions of crystal orientations in the sintered Li$_2$TiO$_3$ samples, the small discrepancy mentioned at the 1.3° may be observed. Except for the differences mentioned above, there is a family of plane not only been modified at the near surface area, but also to a depth of 750 nm. The relative intensity between peak (110) with peak (002) decreases at incidence angles 0.1°, 0.5° and 0.7°. This decrease means that the family of plane (110) has been damaged by D ions in the whole D implanted area.

In conclusion, the implanted D ions on the sintered Li$_2$TiO$_3$ samples have modified the near surface region to a depth around 150 nm, but did not significantly change the crystal structures in the D implanted and bulk areas. The modification indicates that surface crystalline structure of monoclinic Li$_2$TiO$_3$ is very sensitive to mechanical or physical processes.

Similar to the realistic case in which the transmutation product T is generated in damaged Tritium Breeding Blanket, the D ions are here bombarded into Ti ion irradiated Li$_2$TiO$_3$ sample. The XRD patterns of the Ti irradiated and D implanted sample shown in Fig. 5.8 change at some depths in comparison to the as-received sample. Firstly, because of the contribution from the bulk area, the XRD patterns at the incidence angle 1.3° do not significantly change, meaning the crystalline features of the main sample is alike, as expected. When focusing on the (002) and (-133) planes at the incidence angles of 0.1°, 0.5° and 0.7°, the absolute intensity of diffraction peak from (002) family of plane is less than the (-133) plane, as shown in Fig. 5.7, while the absolute intensity of (-133) plane drops considerably and is much less than the absolute intensity of the (002) plane in the irradiated and implanted sample as shown in Fig. 5.8. The later situation indicates that the family of crystal plane (-133) was modified and damaged by the accelerated Ti and D ions to around a depth of 800 nm. Lastly, the peak representing crystal planes (262) became prominent in the irradiated and implanted sample’s XRD patterns. At the incidence angles 0.1° and 0.5°, the (262) peak becomes the highest peak in the XRD patterns in contrast with the case in the Fig. 5.7, in which the (262) peak appears weak. Moreover, in Fig. 5.8, from the incidence angle 0.5° to 0.7°, there is a significant drop at peak (262), while the absolute intensities of the other peaks almost remain the same. Combined with the two observations illustrated above, crystal planes (002) and (-133) have been damaged a lot due to the Ti irradiation and D implantation to around a depth of 650 nm, which is in good agreement with the vacancy distribution area in Fig. 3.2.

To sum up, the crystal pattern of the bulk area after D implantation and Ti irradiation remains alike to the as-received sample, as expected. In the D implanted and Ti irradiated region, particular family of crystal planes are damaged. Reasons may be related to the direction of the incident ion beams resulting in the selectively damaged planes.
5.2 Transmission electron microscopy

Transmission electron microscopy (TEM) is a unique tool in characterizing materials crystal structures and microstructures simultaneously by diffraction and imaging techniques. TEM images show internal structures of specimens with magnification up to 1,000,000 times in viewing structures with atomic resolution. The TEM reveals levels of details and complexity inaccessible by optical microscopy because it uses a beam of energetic electrons rather than visible light. It is a microscopy technique whereby a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through, bombarding with the atoms then diverted and scattered at specific angles. An image is formed from the interaction of the electrons transmitted through the specimen; the image is magnified by a set of lenses and focuses on an imaging device, such as a fluorescent screen emitting light when hit by electrons, on a photographic film, or to be detected by a sensor such as a CCD camera.

5.2.1 Transmission electron microscope

Light microscopes are limited by the physics of light to 500x or 1000x magnification and a resolution of 0.2 micrometers, which is imposed by the wavelength of visible light. Electron microscopes are scientific instruments that use a beam of energetic electrons to examine objects on a very fine scale due to the wave-particle duality of electrons. The wavelength of electrons is given in the de Broglie hypothesis as shown in Equ. 5.3.

\[
\lambda = \frac{h}{p}
\]  

(5.3)

where \( h \) is Planck constant, and \( p \) is the momentum of the electron. Through the use of an electron microscope it is possible to see things that normally not be able to see with naked eyes and has greater magnification than light microscope.

A schematic diagram and an example of a modern transmission electron microscope is illustrated in Fig. 5.9. The electron gun column is consisted of an electron gun assembly at the top, a column filled with a set of electromagnetic lenses, sample port and airlock, a set of apertures (including condensor aperture, objective aperture and selected area aperture) which can be moved in and out of the electron column according to different situations. The whole electron column must be conserved in a high vacuum level equipped with multiple pumping system, due to the short range of electrons in air.
5.2 Transmission electron microscopy

Figure 5.9: A generalised cut-away diagram of internal structure of a transmission electron microscope alongside an example of a modern instrument [23]

Viewing from the top to bottom, the first component is the electron gun. An electron gun (also called electron emitter) is an electrical component that produces an electron beam that has a precise kinetic energy, most often used in television sets and computer displays and in other instruments. Electrons are generated by the electron source, and then accelerated towards a positively charged anode, causing the negatively charged electrons to accelerate towards it. The more highly charged the anode is, the faster the electrons travel, and so a thicker specimen can be viewed. In an electron microscope, the electron gun is usually positioned at the top of the instrument column, which is reverse to the case in a conventional optical microscope, just because it’s more practical and convenient to see the image with this arrangement. Different with the lense in light microscopes which is made of glass, electromagnetic lenses are used in the transmission electron microscope owing to the confinement and focus of the electron beam by them. The electromagnetic lenses are designed to act in a manner emulating that of an optical lense, by focusing parallel rays at some constant focal length. Lenses may operate electrostatically and magnetically. Normally, there are condensor lense, objective lense and projector lense, in which condensor lense controls the size and intensity of the beam hitting the sample and the objective lense and the projector lense control the magnification. Apertures consist with metallic plates with holes inside which only allow
specific electron passing through the holes, while the other are prevented by the plate. Especially, the objective aperture is located at the back focal plane of the objective lense to cancel out the deflected electrons then increases the contrast when doing imaging. Deflectors are devices that can tilt or parallel move the electron beam to obtain a beam at a specific incident angle and the stigmators are used to correct the astigmatism of the lenses in a TEM.

![Image of sample holder](image1)

Figure 5.10: One type of sample holder. [23]

In order to maintain the high vacuum condition in the electron column, the sample holder is designed in a way including air locks that allows the insertion of the sample into the vacuum chamber and at the same time minimizes the pressure influence on other components of the microscope. When doing TEM analysis, the sample is put on small metallic grids which is normally a circular disc 3 mm in diameter with small holes inside as shown in Fig. 5.11. Usually, the holes are not hollow but coated by some kind of film, most commonly carbon film. As so, when the sample is a solution based particle, like nanoparticle of somesort, the solution can be dropped onto the grid and the particles will stay on the carbon film, and they will be easily monitored on the TEM.

![Image of sample grids](image2)

Figure 5.11: Sample grids scattered on a Petri dish and zoomed in one grid. [23, 24]

The sample grid needs to be mounted onto the sample holder and one type of the sample holders is shown in Fig. 5.10. At the top of it, there are one or
two wells depending on different types, at which the sample grid is screwed into by a flange or a ring and hold it securely in place. When the sample holder is in the electron column, it is imperative that the sample grid does not fall off from the sample holder. After the sample grid is located onto the sample holder, the holder then is inserted into the sample port for further analysis.

5.2.2 Electron diffraction

Incident electrons scattered by the atoms in the specimen in an elastic fashion follow Bragg’s law. Similar angle of the electrons from the plane of same atomic spacing yields information about the orientation, atoms arrangements and phases present. Both electron diffraction and x-ray diffraction are caused by constructive interference of scattered waves, and the same fundamental law can be applied for the interpretation of diffraction patterns. Electrons and X-ray are diffracted by the period crystal structure in the lattice complying with Bragg’s condition in Equ. 5.1. However, there are several discrepancies between these two. Firstly, the electrons are scattered by the Coulomb potential interacting with the positive nucleus, while the diffraction of x rays results from the interaction with the electron cloud. What’s more, as for polycrystalline samples, both the electron diffraction and X-ray diffraction will obtain several concentric rings, while what’s special for a TEM is that it has a selected area aperture which can selects out a smaller diffracted region to a single crystal. Lastly, the wavelength of electrons (e.g.1.97 pm for a 300 keV electrons) is much shorter than that of X-rays (about 100 pm), therefore, the radius of Ewald sphere is much larger and more reflections are observed by ED than by XRD.

The imaging of the specimen in conventional microscope is formed selectively allowing only the transmitted beam (Bright Field Imaging) or one of the diffracted beams (Dark Field Imaging) down to the microscope by means of aperture. And the origin of the image contrast is the variation of intensities of transmitted and diffracted beams due to the differences in the microstructural features in the specimen. As is introduced above, the intermediate lense it not only responsible for adjusting the magnification but also switching between the magnified image operation and the electron diffraction operation. The simplified light paths are illustrated as in Fig. 5.12. The light path shown on the left side in Fig. 5.12 tells how the magnified image of the sample is projected on the fluorescent screen. In an attempt to do so, the object plane of the intermediate lense must coincide to the image plane of the objective lense. In another case, if the object plane of the intermediate lense overlaps with the back focal plane of the objective lense, a clear diffraction pattern can be achieved on the screen as shown on the right light path in Fig. 5.12. On accounting of the fixed locations of all the lenses, the switch operations are implemented by altering the current inside the electromagnetic lenses resulting in different focal lengths, while with unchanged image length $L_2$. 
5.2 Transmission electron microscopy

As mentioned above, one of the significant advantages of transmission electron microscope is the selected area electron diffraction (SAED). SAED is referred as 'selected' because the user can easily choose from which part of the specimen to obtain the diffraction pattern with the help of the selected area aperture. The selected area aperture is just beneath the objective aperture on the TEM column, which can be inserted into the beam path, blocking the undesired diffraction electrons but letting the small choosed fraction pass through. Normally, there are different size of holes on the selected area aperture, by moving the aperture hole under the section of sample needed to be examined, this particular area is selected by the aperture and only this section will contribute to the SAED diffraction pattern. SAED is quite useful for identifying crystal structures and examine crystal defects. And it is important for examining polycrystalline specimen. because when the electron diffraction pattern comes from more than one crystal, it may become hard to analyze the atom arrangements inside a single crystal, then it is really useful to select only one crystal at a time which can be realized by SAED if the aperture is small enough and the crystal is large enough. And also selecting two crystals at a time makes it possible to examine the crystalline orientations between them.

5.2.3 TEM sample preparation

Normally, the specimen under the TEM examination is demanded to be under 200 nm in thickness because of the absorption of electron in the material. Even though elevating the accelerating voltage can reduce the absorption ef-
fected, it will increase the unwanted radiation damage to the material. Because of different material phases: liquid, solid, solution based nanoparticles and so on, the sample preparation processes are quite distinct. The studied material here is solid monoclinic $\text{Li}_2\text{TiO}_3$, the TEM sample preparation process was carried out following the steps as illustrated in Fig. 5.13. First, the hard sample blocks are cutted into slices by a diamond-coated saw blade to a thickness around 300 um; then the slide is shaped into a circle with 3 mm in diameter by an ultrasonic disc cutting technique. The now disc with 3 mm in diameter and 300 um in thickness requires to be thinned by grinding and polishing techniques to a thickness of 100 um, right after which a dimple grinding wheel is implemented to thin out the center of the disc from one side or both sides to 20 um. Lastly, the center of the depression needs to be further thinned by the ion milling technique, which uses energetic Argon ions bombarding at a low angle (smaller than $10^\circ$) until the center area is electron transparent.

Specifically in our case, because the interested region of $\text{Li}_2\text{TiO}_3$ is near surface, the surfaces of two implanted or irradiated $\text{Li}_2\text{TiO}_3$ cross section samples are faced to each other and then glued together by some metal organic compound. Then the sample is thinned following the processes shown in Fig. 5.13.

![Figure 5.13: Schematic processes of TEM sample preparation. [25]](image)

### 5.2.4 TEM results

The D implanted and Ti irradiated sample has been examined under a transmission electron microscope. The TEM image and electron diffraction patterns at different locations are illustrated in Fig. 5.14. The whole image shows a rectangular area about 1600 nm in length and 1100 nm in width. The left down triangular area is the TEM image of the metal glue used in the TEM sample preparation process, which helps locate the sample surface labeled with “irradiation surface” in the figure. From the surface to a depth of 1000 nm, the TEM image can be roughly divided into three areas and each one of them is presented with their selected area electron diffraction patterns. According to
Elisabetta Carella and Maria Gonzalez [15], the average grain size of $Li_2TiO_3$ is around 2 $\mu$m; however, the selected area of the presented electron diffraction patterns is limited in a circle with diameter smaller than 100 nm. XRD patterns result from x ray diffractions of polycrystalline $Li_2TiO_3$, but with the SAED technique it’s possible to observe crystal structure inside a grain. The first area is from the surface to a depth around 200 nm, in which the selected area electron diffraction pattern contains a bright dot in the center with a blurred bright circle around, indicating that the crystal structure is almost damaged because of D implantation and Ti irradiation. Another area ranges from 800 nm to 1200 nm in depth, and its electron diffraction pattern consists of series of periodic bright dots which implies the crystal structures inside this area as expected for the bulk sample. The last area is from a depth of 200 nm to 800 nm, in which the pattern of the crystalline structure is modified, few of the bright dots being left visible. Because each of the bright dot represents a family of plane in the real crystal structure, many planes has been damaged by Ti ions and D ions in good agreement with the Ti ion main distribution area predicted by SRIM.

Figure 5.14: TEM images and electron diffraction patterns of D implanted and Ti irradiated $Li_2TiO_3$ sample. [21]
5.3 Discussion

The SRIM simulation predicts that the non-coincident D implantation and Ti irradiation sample will present both a peaked D distribution at a depth of 750 nm and a peaked amount of vacancy distribution at a depth of 450 nm. The XRD patterns of D implanted and Ti irradiated sample at incidence angles 0.1° and 0.5° behave quite differently with the ones of as-received $Li_2TiO_3$ sample, indicating a modified and damaged area from surface to a depth of 650 nm, which is in good agreement with the SRIM prediction. Also, the electron diffraction patterns at the area from 200 nm to 800 nm present a bright dot in the center with two blurred bright dots around, implying the modification of crystalline structure in this region, further confirming the damage induced by the Ti irradiation and D implantation consisting with XRD results and SRIM simulation.

The D distribution and defects in the D implanted $Li_2TiO_3$ sample are simulated by SRIM program as shown in Fig. 3.5. The D distribution peaks at a depth of 750 nm, however, according to the nuclear reaction analysis (NRA) results in [15], the D profile is a descending line which peaks at the sample surface. And it’s necessary to mention that the D implanted sample processed in Ref. [15] is exactly the same as the one used in the non-coincident case experiment mentioned above. So it is reasonable to make a comparison with the two results. This discrepancy between the NRA results and the simulated depth profile by SRIM may result from the D release behaviour at room temperature and a lack of parameters taken into account for the SRIM simulation. The SRIM simulation is not considering the crystalline modifications and formation of vacancies due to D implantation, which could explain the easier D diffusion even at room temperature. Therefore, some experiments are needed to validate SRIM simulations. The XRD patterns shown in Fig. 5.7 and electron diffraction pattern in Fig. 5.14 indicate that the crystal structure of surface area below the depth of around 200 nm is modified by the D implantation, while crystal structure at a deeper depth almost remain the same. The change of the XRD patterns at the surface is consistent with the NRA results, that the accumulation of D atoms have modified the crystal structure in the surface. The selected area electron diffraction pattern of D implanted and Ti irradiated $Li_2TiO_3$ sample at a depth within 200 nm presents only a bright circle in the center, indicates the crystal structure within a 100 nm diameter circle is almost damaged. However, the XRD pattern at incidence angle 0.1° shows there is still partial crystal structure preserved at a large scale.

For further diffusion studies, the D implanted and Ti irradiated $Li_2TiO_3$ sample should be examined by the thermal desorption spectroscopy (TDS) to study the deuterium release behaviour [26]. According to study by M. Oyaidzu and Y. Morimoto [27, 28], the relationship between thermal release mechanism of tritium and thermal annihilation kinetics of radiation defects in thermal neutron-irradiated $Li_2TiO_3$ indicates that the annihilation of oxygen...
vacancy could play an important role in the tritium release process, and the oxygen vacancy could work as a tritium-trapping center in which the diffusion of point defects in $Li_2TiO_3$ will benefit the bulk diffusion of tritium. As simulated in the SRIM results, oxygen vacancies are the major defects in the D implanted and Ti irradiated $Li_2TiO_3$. As tritium and deuterium are both isotopes of hydrogen, it is naturally to guess that the annihilation of oxygen vacancy defects can also work as a deuterium trapping site, which will contribute to the deuterium release process. The electron spin resonance (ESR) method can be employed to follow the annihilation behavior of the radiation defects in thermal treatment, and compare the result with the thermal desorption spectrum to further analyze the deuterium release mechanism.

Depending on the results obtained for the non-coincident peaked D implantation and Ti irradiation $Li_2TiO_3$ sample, reasonable speculations can be achieved for the coincident peaked case and the uniform case. The XRD patterns and electron diffraction of the coincident D implanted and Ti irradiated case will behave alike to the non-coincident case, because the similarity between them except for a deeper Ti irradiated depth. However, the uniform D implantation and Ti irradiation in the $Li_2TiO_3$ solid breeder case should be different, which is proposed to simulate a more realistic fusion reactor environment situation. The experimental results for the uniform case should be expected in these ways: The XRD patterns and electron diffraction pattern will indicate that the crystal structures from the surface to the farthest depth that Ti ion can reach, is almost damaged by Ti ions and D ions. The D distribution profile characterized by NRA technique will present as a descending line from the surface to the bulk area of $Li_2TiO_3$ solid breeder, rather than a flat line. The predicted accumulation of D ion at the near surface region will benefit the deuterium release process, which will contribute to the collecting and recycling of deuterium in further studies.

When considering the recycling of tritium back to the fusion reaction chamber in an engineering point of view, the tritium blanket system must collect the generated tritium in the tritium breeding blanket and then inject the tritium fuel after several processes i.e. extraction, purification, injection. So the total efficiency of the tritium blanket system becomes a quite important issue to be examined. As studied by T.Kinjyo and M.Nishikawa et al [29, 30, 31], tritium release behaviour not only depends on the tritium diffusion inside the grain, but also transfer at surface layer and grain surface reaction as isotope exchange. Except for varying the thermal desorption temperature to achieve the deuterium desorption profile as a function of solid breeder temperature, the dependence of deuterium release rate on purge gas species, sweep gas flow rate and hydrogen content in sweep gas should be studied in the uniform D implanted and Ti irradiated $Li_2TiO_3$ solid breeder, to collect enough engineering data to obtain a most effective tritium extraction system.
Chapter 6

Conclusions

In an attempt to understand the mechanisms for the light ion (H, D, T ions) transport in a fusion nuclear environment, three different sets of experiments on fusion candidate lithium metatitanate ($\text{Li}_2\text{TiO}_3$) are simulated: D was the selected hydrogenic ion to be implanted while a Ti ion beam was considered for irradiation to produce the structural damage. Just the non-coincident case was then implemented experimentally and the sample characterized by means of GIXRD and TEM+SAED techniques to analyse the irradiation effects and the degree of agreement between simulation and experiments.

The SRIM simulated damage distribution in non-coincident peaked D-implanted and Ti-irradiated $\text{Li}_2\text{TiO}_3$ is consistent with the XRD patterns. When compared with the as-received situation, the XRD experimental patterns suggest major damage area below surface down to 600nm, indicating that crystal structure has been damaged by the bombarding energetic Ti ions. In the first 200 nm below surface, the XRD resultant features suggest that the crystal structure has been modified by the accumulation of D atoms there.

The TEM images and SAED patterns from surface down to predicted ion stopping ranges of the non-coincident peaked D implanted and Ti irradiated $\text{Li}_2\text{TiO}_3$ sample further confirm the different grade of distorted crystal structure. The SAED patterns obtained at increasing depths below 500nm show that the initial monoclinic crystalline structure was seriously damaged due to mainly the heavy Ti ion bombardment.

In summary, the SRIM prediction is in good agreement with both the XRD results and the SAED patterns, so the SRIM program can be implemented as a useful tool to simulate ion implantation and irradiation effect on solid breeder material $\text{Li}_2\text{TiO}_3$. However, unexpected behaviours, i.e. the experimental D concentration distribution, are observed when compare with NRA technique results. The reason should be explained as a consequence of a lack of parameters taken into account for the SRIM simulation. The simulation is not considering the crystalline modifications and formation of vacancies due to D implantation, which could explain the easier D diffusion even at room temperature. For further studies on the D diffusion and release process, analytical techniques should be implemented to better understand the features of
$Li_2TiO_3$ breeder material after implantation and irradiation. The XRD and TEM techniques are essential to analyze the structural characterization of $Li_2TiO_3$ breeder material before and after implantation and irradiation. The D depth profiles can be characterized by means of Resonance Nuclear Reaction Analysis (RNRA) to follow the evolution of deuterium diffusion. Electron spin resonance (ESR) technique can be applied to follow the annihilation behavior of Ti irradiated defects along with thermal desorption spectroscopy (TDS), to determine the correlation between annihilation of oxygen vacancy and deuterium release behavior. The relationship between deuterium release rate and purge gas species, sweep gas flow rate and hydrogen content in the purge flow is interesting to optimize the deuterium release system.
Bibliography


[26] M. Gonzalez et al., In press in Fusion Engineering and Design.


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...
Declaration in lieu of oath

Herewith I declare in lieu of oath that I have prepared this thesis exclusively with the help of my scientific teachers and the means quoted by them.

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