Crystal Structure of Non-stoichiometric Compound Li$_{2-x}$TiO$_{3-y}$ under Hydrogen Atmosphere

Tsuyoshi Hoshino* (1), Masaru Yasumoto (2), Kunihiko Tsuchiya (1), Kimio Hayashi (1), Hidetoshi Nishimura(3), Akihiro Suzuki (3), Takayuki Terai (2)

1. Introduction
Lithium titanate (Li$_2$TiO$_3$) is one of the most promising candidates for solid breeder materials. However, Li$_2$O deficient on Li$_2$TiO$_3$ is generated by Li vaporization and burnup in fusion reactor. In the present paper, the non-stoichiometric composition of Li$_2$TiO$_3$ has been extensively investigated by means of atmosphere-controlled high temperature mass spectrometry and thermogravimetry.

2. Experimental
In the case of the Li$_2$TiO$_3$ samples used for the present study, Li$_2$CO$_3$ and TiO$_2$ powders were mixed in the proportions corresponding to the molar ratio (Li$_2$O/TiO$_2$) of either 1.00, 0.95, 0.90 or 0.80. These samples are designated as L100, L95, L90 and L80, respectively.

In order to evaluate the vaporization property of nearly stoichiometric Li$_2$TiO$_3$, the vapor pressures of the Li$_2$TiO$_3$-D$_2$, Li$_2$TiO$_3$-D$_2$O and Li$_2$TiO$_3$-O$_2$ system were measured with an atmosphere-controlled high temperature mass spectrometer.

On the other hand, in non-stoichiometric measurement, the apparatus used was a thermogravimetry Model Cahn-2000 of Cahn Instruments, Inc., USA. The weight changes were measured to an accuracy of ±0.01mg for samples 0.3-0.5g.

3. Results
3.1. Vaporization Property
In order to evaluate the vaporization property of nearly stoichiometric Li$_2$TiO$_3$, the vapor pressures of the Li$_2$TiO$_3$-D$_2$ system were measured with an atmosphere-controlled high temperature mass spectrometer. The vapor pressure of Li-containing vapor species gradually rose by D$_2$ and D$_2$O addition at a constant temperature. The pressure of Li-containing species decreased in the following order:

\[ P_{Li}^{total} (D_2O) > P_{Li}^{total} (D_2) > P_{Li}^{total} (Vacuum) > P_{Li}^{total} (O_2) , \]
influencing the partial pressure of $O_2$, $D_2$ and $D_2O$.

3.2. Non-Stoichiometry

In thermogravimetry, the mass of $Li_2TiO_3$ was found to decrease with time in the hydrogen atmosphere. Then, the color was observed to change from white to dark blue as well. This color-change indicates that the oxygen content of the sample decreased, suggesting the change from $Ti^{4+}$ to $Ti^{3+}$. Furthermore, L80 have more oxygen deficient than the other kinds of $Li_2TiO_3$, so that the order of oxygen deficient was as follows, $L80 > L90 > L95 > L100$, corresponding to the inverse order of molar ratio of the samples.

4. Conclusions

The overall behavior suggests not only oxygen deficient but also lithium oxide deficient defect formation. Thus, the doubly non-stoichiometric composition, $Li_{2-x}TiO_{3-y}$, has been confirmed.

*Corresponding author
Tsuyoshi Hoshino
Blanket Irradiation and Analysis Group, Directorates of Fusion Energy Research, Japan Atomic Energy Agency, 4002, Narita-cho, Oarai-machi, Higashi Ibaraki-gun, Ibaraki, 311-1393, Japan
E-mail: hoshino.tsuyoshi@jaea.go.jp
1.1. Background

Solid Breeder Material - Li$_2$TiO$_3$ -

The tritium, which is generated by the reaction between lithium and neutrons, should be extracted with inert sweep gas efficiently in order to establish the tritium fuel cycle.

It has been proposed to mix hydrogen into the inert sweep gas for the purpose of the enhancement of the tritium release rate from the surface of the breeder material.

Non-stoichiometry

However, its structure in regard to non-stoichiometric composition (Li$_{2-x}$TiO$_{3-y}$) has not been well established yet.

Recently, mass of the Li$_2$TiO$_3$ was decreased with time in a hydrogen atmosphere generating O deficient of the sample.

1.2. Purpose

O deficient

The influence of TiO$_2$ addition on the compositional property of Li$_2$TiO$_3$ under hydrogen and oxygen atmosphere has been further investigated by means of thermogravimetry, XRD and so on.

- The structure and the non-stoichiometry of Li$_2$TiO$_3$ added with some different oxides have been extensively investigated.

Li deficient

The observed vaporization characteristic of Li$_2$TiO$_3$ under these conditions is presented here.

- The sum of the partial pressures of Li-containing species.
- The temperature dependence of Li vapor pressure indicated that Li-containing species
2.1. Sample

Powder mixtures of Li$_2$CO$_3$ and TiO$_2$ were calcined under air at 1223K for 10 hr. The resulting products were isostatically pressed at 150MPa and were sintered at 1323 K for 24 h.

<table>
<thead>
<tr>
<th>Sample Name</th>
<th>Molar ratio Li$_2$O/TiO$_2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>L100</td>
<td>1.00</td>
</tr>
<tr>
<td>L95</td>
<td>0.95</td>
</tr>
<tr>
<td>L90</td>
<td>0.90</td>
</tr>
<tr>
<td>L93.8</td>
<td>0.938</td>
</tr>
<tr>
<td>L80</td>
<td>0.80</td>
</tr>
</tbody>
</table>

L100(Li$_2$O/TiO$_2$=1.00)  \[1.00\text{Li}_2\text{CO}_3 + 1.00\text{TiO}_2 \rightarrow \text{Li}_2\text{TiO}_3\]

L95(Li$_2$O/TiO$_2$=0.95)  \[0.95\text{Li}_2\text{CO}_3 + 1.00\text{TiO}_2 \rightarrow \text{Li}_{1.9}\text{TiO}_{2.95}\]

L90(Li$_2$O/TiO$_2$=0.90)  \[0.90\text{Li}_2\text{CO}_3 + 1.00\text{TiO}_2 \rightarrow 0.929\text{Li}_{1.876}\text{TiO}_{2.938} + 0.014\text{Li}_4\text{Ti}_5\text{O}_{12}\]

L80(Li$_2$O/TiO$_2$=0.90)  \[0.90\text{Li}_2\text{CO}_3 + 1.00\text{TiO}_2 \rightarrow 0.744\text{Li}_{1.876}\text{TiO}_{2.938} + 0.051\text{Li}_4\text{Ti}_5\text{O}_{12}\]

2.2 XRD and Thermogravimetry

**XRD**: RINT2000 of Rigaku Co.

XRD powder patterns were obtained using a beam of CuKa radiation (\(\lambda = 1.5418\ \text{Å}\)) generated.
Voltage: 40 kV, Current: 200 mA, 2\(\theta\) = range 10-100\(^\circ\), Scanning speed = 1.5min\(^{-1}\), Slit width = 0.01\(^\circ\)

**Thermogravimetry**: Model Cahn-1000 of Cahn Instruments, Inc. USA.

Prior to each run, the sample was kept in vacuum at 873 K for 8 hr to remove LiOH.

<table>
<thead>
<tr>
<th>Temperature</th>
<th>1273K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atmospheres</td>
<td>Reduction : Ar95%-H$_2$5% (30h) Oxidation : Ar-O$_2$ (20h), O$_2$ (3h)</td>
</tr>
</tbody>
</table>
2.3 High-temperature mass spectrometer

<table>
<thead>
<tr>
<th>Condition</th>
<th>Principle</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device</td>
<td>Atmosphere-controlled high-temperature mass spectrometer</td>
</tr>
<tr>
<td>Preprocessing of sample</td>
<td>Sample was kept in vacuum for 10 h at 873K to remove LiOH.</td>
</tr>
<tr>
<td>Shape of sample</td>
<td>Powder (2~3 μm)</td>
</tr>
<tr>
<td>Temperature</td>
<td>973 ~ 1473K</td>
</tr>
<tr>
<td>Atmosphere</td>
<td>• Vaccum • O₂ • D₂ • D₂O</td>
</tr>
</tbody>
</table>

Ionizing electrons were accelerated to 30 eV.

“Vapor Species”, “Partial Pressures”

3.1. Lithium oxide deficient Li₂TiO₃

- In case of L90 and L80, Li₄Ti₅O₁₂ peaks appeared.
- L95 and L93.8 were nearly the same as that of L100, where no presence of Li₄Ti₅O₁₂.

- L95, L93.8: nonstoichiometric compound Li₂₋ₓTiO₃₋₀.₅ₓ
- L90, L80: mixture compounds of LiₓTiO₃₋₀.₅ₓ and Li₄Ti₅O₁₂

L100(Li₂O/TiO₂=1.00) 1.00Li₂CO₃ + 1.00TiO₂ → Li₂TiO₃
L95(Li₂O/TiO₂=0.95) 0.95Li₂CO₃ + 1.00TiO₂ → Li₁₋₀.₀₅TiO₂.₉₅
L90(Li₂O/TiO₂=0.90) 0.90Li₂CO₃ + 1.00TiO₂ → 0.929Li₁₋₀.₀₇₆TiO₂₋₀.₀₃₈ + 0.014Li₄Ti₅O₁₂
L80(Li₂O/TiO₂=0.90) 0.90Li₂CO₃ + 1.00TiO₂ → 0.744Li₁₋₀.₀₇₆TiO₂₋₀.₀₃₈ + 0.051Li₄Ti₅O₁₂

Fig. X-ray diffraction patterns of Li₂TiO₃
3.2. Oxide deficient Li$_2$TiO$_3$

The oxygen content of the sample decreased, suggesting change from Ti$^{4+}$ to Ti$^{3+}$ under the reducing atmosphere.

Peaks of LiTiO$_2$ appeared in the X-ray patterns of L80 and Li$_4$Ti$_5$O$_{12}$ kept under the reducing condition. But peaks of LiTiO$_2$ did not appear in the X-ray pattern of L95.

**Fig.** X-ray diffraction patterns of L95, L80 and Li$_4$Ti$_5$O$_{12}$ kept in reducing condition as compared to LiTiO$_2$.

Therefore

**Reaction equation in reduction at 1073K.**

\[
\begin{align*}
L100, L95 & \rightarrow Li_{2-y}TiO_{3-y} \\
L90, L80 & \rightarrow Li_{1.876}TiO_{2.938} (L93.8) + Li_4Ti_5O_{12} + LiTiO_2
\end{align*}
\]

4.1. Measurement of thermogravimetry

Mass of Li$_2$TiO$_3$ was found to decrease with time in the atmosphere of hydrogen, then to increase after the change of the atmosphere from hydrogen to argon-oxygen mixed gas and then to oxygen.

However

The mass of Li$_2$TiO$_3$ did not recover the weight of pre measurement, 288.5mg.

**Fig.** Weight change of 95Li$_2$TiO$_3$ by thermogravimetry

Vapor species were Li, LiOH, Li$_2$O, LiO, D$_2$O and D$_2$

Li$_2$O deficient as much as 0.982mg was attributed to vaporization while O deficient of 1.175mg to valency change Ti$^{3+}$/Ti$^{4+}$ caused by reduction.
4.2. Quantity of O deficient

- The Molar fraction of oxygen deficient increased as the molecular rate Li₂O/TiO₂ decreased, and a linear relation was realized between them.

The calculation result of the molar fraction of oxygen deficient of Li₂TiO₃.

The order of oxygen deficient was as follows, L80 > L90 > L95 > L100

4.3. Color of Li₂TiO₃

(a) 95Li₂TiO₃ Pellet
(b) Reduction
(c) Oxidation

The color of L95 became deeper than the color of L100, it is thought that there is a relation with the quantity of an oxygen defect. Similar behavior was confirmed on other samples, L90 and L80.
4.4. XRD (Non-stoichiometry)

1. Peaks of LiTiO$_2$ → no appearance

2. Peaks of 95Li$_2$TiO$_3$ sample kept under reducing condition had been shifted to smaller 2θ direction compared to those before reduction. This shift was ascribed to the fact that the radius of Ti$^{3+}$ is larger than that of Ti$^{4+}$.

These behaviors suggest that, in case of such a reducing condition, 95Li$_2$TiO$_3$ sample is single phase non-stoichiometric compound, Li$_{2-x}$TiO$_{3-y}$.

4.5. Limit of non-stoichiometry

1. The chemical formula of L95 by reduction and oxidation was changed to L93.8.

2. In case of L93.8, the peak of Li$_4$Ti$_5$O$_{12}$ did not appear.

3. The measured value agrees well with the calculated value (Fig), as a result of molar fraction of oxygen deficient of L80, which was calculated from the molar fraction of oxygen deficient of L93.8 and Li$_4$Ti$_5$O$_{12}$.

The limit of molecular formula was set to Li$_{1.876}$TiO$_{2.938}$ (L93.8).
4.6. Reduction temperature

Weight change of L90 was measured in the temperature range from room temperature to 1273K by reduction, in order to investigate the temperature at which reduction occurs.

1. The weight of L90 gradually decreased, generating O-vacancy from 603K by reduction.

2. Above 803K, the weight of L90 decreased quickly with a strong reduction reaction.

At 803K or above, it became clear that there is no influence of temperature on the molar fraction of oxygen deficient.

![Graph showing weight change vs. temperature](image)

Fig. Comparison between the measured and calculated values of the molar fraction of O deficient of L80.

5.1. Partial Pressures - Vacuum, O₂ -

**Vacuum**

**O₂**

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Vapor Species</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li</td>
<td>Li(g)</td>
</tr>
<tr>
<td>O₂</td>
<td>O₂(g)</td>
</tr>
<tr>
<td>Li₂O</td>
<td>Li₂O(g)</td>
</tr>
<tr>
<td>LiO</td>
<td>LiO(g)</td>
</tr>
</tbody>
</table>

**Vapor Species**

- Li(g)
- O₂(g)
- Li₂O(g)
- LiO(g)

Introduction of O₂ caused the increase in the oxygen potential, and then Li(g) vaporization was restrained.
5.2. Partial Pressures - D₂, D₂O -

- **D₂**
  - Symbol: Li₂TiO₃
  - Vapor Species: D₂, D₂O, Li, LiOD

- **D₂O**
  - Symbol: Li₂TiO₃
  - Vapor Species: D₂, D₂O, Li, LiOD

Vapor Species
- D₂(g)
- D₂O(g)
- Li(g)
- LiOD(g)

Introduction of D₂ and D₂O caused the decrease in the oxygen potential, and Li(g) vaporization was enhanced.

5.3. Pressures of Li-containing Species

**Pressures of Li-containing species (P_{Li}^{total})**

- **Vacuum, O₂**
  - \[ P(Li) = \frac{K_a}{\sqrt{P(O_2)_{1/2}}} \]
  - Li-containing species appeared above 1200K

- **D₂, D₂O**
  - \[ P(Li) = \frac{K_b}{\sqrt{P(O_2)_{1/2}}} = \frac{K_aK_dP(D_2)}{P(D_2O)} \]
  - Li-containing species appeared above 973K
5.4. Calculation of Amount of Evaporation

Calculation condition: 1073K (1%H₂-He), 1.5 year, 20% Burnup

<table>
<thead>
<tr>
<th>Chemical formulae</th>
<th>Weight Loss of Li by Burnup (mol)</th>
<th>Weight Loss of Li by Evaporation (mol)</th>
<th>O Deficiency by reduction (mol)</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂TiO₃ (1mol)</td>
<td>0.40</td>
<td>0.056</td>
<td>0.069</td>
<td>0.74Li₁₈₇TiO₂₉₃₃ + 0.05aLi₄Ti₅O₁₂ + bLiTiO₂</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Chemical formulae</th>
<th>Weight Loss of Li by Burnup (mol)</th>
<th>Weight Loss of Li by Evaporation (mol)</th>
<th>O Deficiency by reduction (mol)</th>
<th>Chemical formulae</th>
</tr>
</thead>
<tbody>
<tr>
<td>Li₂O (1mol)</td>
<td>0.40</td>
<td>0.12</td>
<td>0</td>
<td>0.74Li₂O</td>
</tr>
</tbody>
</table>

- The weight Loss of Li of Li₂TiO₃ is less than that of Li₂O.

6. Conclusions

In order to examine possible non-stoichiometry of Li₂TiO₃, the composition of Li₂TiO₃ has been investigated by means of thermogravimetry, X-ray diffractmetry (XRD) and Atmosphere-controlled high-temperature mass spectrometer.

Non-stoichiometry

1. The color was observed to change from dark blue to the initial color, white, after the change of the atmosphere from hydrogen to oxygen.

2. Mass of Li₂TiO₃ was found to change as observed by means of thermogravimetry. These results for L100 and L95 indicate not only oxygen deficient but also lithium oxide deficient defects formation.

The doubly non-stoichiometric composition, Li₂₋ₓTiO₃₋ᵧ, has been confirmed.
6. Conclusion

**Vapor Species**
- Vacuum, O₂ atmosphere: Li(g), Li₂O(g), LiO(g) and O₂(g).
- D₂, D₂O atmosphere: Li(g), LiOD(g), D₂(g) and D₂O(g).

**Partial Pressures of Li-containing Species**
The sum of the partial pressures of Li-containing species was calculated. Its order in these atmospheres was as follows:

\[ \text{O}_2 < \text{Vacuum} \approx \text{Ar} \ll \text{D}_2 \approx \text{D}_2\text{O}. \]

**The Color of the Sample**
After the vapor pressure measurement in the D₂ atmosphere, the color of the sample was found to have been changed from white to **dark blue**. (This behavior suggests the formation of oxygen deficient defects in reduction atmosphere.)