



Non-stoichiometry of Li_2TiO_3 under hydrogen atmosphere conditions

Tsuyoshi Hoshino ^{a,*}, Hiroshi Kawamura ^b, Masayuki Dokiya ^c,
Yoich Takahashi ^d, Takayuki Terai ^e, Michio Yamawaki ^f

^a *Oarai Research Establishment, Department of JMTR Project, Japan Atomic Energy Research Institute, Blanket Irradiation and Analysis Laboratory, 3607, Narita-cho, Oarai-machi, Higashi Ibaraki-gun, Ibaraki 311-1394, Japan*

^b *Naka Fusion Research Establishment, Japan Atomic Energy Research Institute, 801-1, Naka-machi, Naka-gun, Ibaraki 311-0193, Japan*

^c *Graduate School of Environment and Information Sciences, Yokohama National University, 79-7, Tokiwadai, Hodogaya-ku, Yokohama 240-8501, Japan*

^d *Department of Applied Chemistry, Chuo University, 1-13-27, Kasuga, Bunkyo-ku, Tokyo, 112-8551, Japan*

^e *Nuclear Engineering Research Laboratory, School of Engineering, The University of Tokyo, 2-22 Shirakata-Shirane, Ibaraki 319-1106, Japan*

^f *Department of Quantum Engineering and Systems Science, Graduate School of Engineering, University of Tokyo, 7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656, Japan*

Abstract

Li_2TiO_3 is one of the most promising candidate solid breeder materials. However, its structural properties have not been established, especially for a non-stoichiometric composition. In the present paper, non-stoichiometric compositions of Li_2TiO_3 have been extensively investigated by means of thermogravimetry, X-ray diffraction and color change observations. For the Li_2TiO_3 samples used in the present study, Li_2CO_3 and TiO_2 powders were mixed in the proportion corresponding to the molecular ratio $\text{Li}_2\text{O}/\text{TiO}_2$ of either 1.00, 0.95, 0.938, 0.90 or 0.80. In thermogravimetry, mass of the Li_2TiO_3 samples was found to decrease with time in a hydrogen atmosphere, then to increase after the change of the atmosphere from hydrogen to oxygen. The color of the samples was observed to change from white to dark blue under a hydrogen atmosphere. These results suggest not only oxygen deficient but also Li_2O deficient defect formation. Thus, the doubly non-stoichiometric composition, $\text{Li}_{2-x}\text{TiO}_{3-y}$, has been confirmed.

© 2004 Elsevier B.V. All rights reserved.

1. Introduction

In D–T fusion reactors the blanket has two roles, to breed tritium (T) and to convert the energy of neutrons into heat. Lithium containing ternary oxides have been proposed as breeder blanket materials. In this respect, Li_2O , LiAlO_2 , Li_4SiO_4 , Li_2ZrO_3 and Li_2TiO_3 have been considered as candidates for tritium breeding [1].

Li_2TiO_3 has been identified as a prominent candidate because of its good tritium release property [2] and its low activation characteristics. However, its structure for a non-stoichiometric composition is not well established. Yamaguchi et al. [3] estimated that Li_2TiO_3 probably had no non-stoichiometric composition range, based on the results of vapor pressure and work function measurements. Later, Hoshino et al. [4] proposed non-stoichiometric compositions such as $\text{Li}_{2-x}\text{TiO}_{3-y}$ from the X-ray diffraction (XRD) test results. More recently, the mass of Li_2TiO_3 was found to decrease in a hydrogen atmosphere, generating an oxygen deficient material [5].

In the present study, the influence of TiO_2 addition on the compositional property of Li_2TiO_3 under

* Corresponding author. Tel.: +81-29 264 8417; fax: +81-29 264 8480.

E-mail address: hoshino@sky.biglobe.ne.jp (T. Hoshino).

hydrogen and oxygen atmospheres has been further investigated by means of thermogravimetry, XRD and other techniques.

2. Experimental

2.1. Sample

Powder mixtures of Li_2CO_3 and TiO_2 were calcined in air at 1223 K for 10 h. The resulting products were isostatically pressed at 150 MPa and were sintered at 1323 K for 24 h. Li_2CO_3 and TiO_2 powders were mixed in the proportion corresponding to the molecular ratios $\text{Li}_2\text{O}/\text{TiO}_2$ of 1.00, 0.95, 0.938, 0.90 or 0.80, in order to examine the effect of the composition of specimens. These samples are designated as L100, L95, L93.8, L90 and L80, respectively, as shown in Table 1. The pellets were crushed to powder of 2–3 μm diameter for the measurements.

2.2. Thermogravimetry and X-ray diffraction

The apparatus used was a thermogravimetry Model Cahn-1000 of Cahn Instruments Inc., USA. Details of weight change measurements by thermogravimetry were described in a previous paper [5]. Changes in stoichiometry were studied at 1273 or 1073 K in reducing atmospheres and at 1073 K in oxidizing atmospheres. Prior to each run, the sample was kept in vacuum at 873 K for 8 h to remove LiOH.

Powder X-ray diffraction patterns were obtained using a beam of $\text{CuK}\alpha$ radiation ($\lambda = 1.5418 \text{ \AA}$) generated with RINT2000 of Rigaku Co. The operational settings for all the X-ray diffraction scans were as follows; voltage: 40 kV, current: 200 mA, 2θ range = 10–80; scanning speed = $1.5^\circ \text{ min}^{-1}$ and slit width = 0.01° .

3. Results

Non-stoichiometric compositions of Li_2TiO_3 has been investigated by assuming the presence of two types

of deficiencies; Li_2O deficient Li_2TiO_3 and O deficient Li_2TiO_3 .

3.1. Lithium oxide deficient Li_2TiO_3

The authors proposed that L95 is a non-stoichiometric compound $\text{Li}_{2-x}\text{TiO}_{3-y}$ [4], and that L90 and L80 are mixture of Li_2TiO_3 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. In order to examine this model, the following specimens were prepared and examined by using XRD technique: L95, L93.8, L90, L80 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$.

Results of XRD analyses are shown in Fig. 1. For the cases L90 and L80, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ peaks (at $2\theta = 35.6^\circ, 43.3^\circ, 43.4^\circ, 53.2^\circ, 57.4^\circ, 62.9^\circ, 63.0^\circ, 66.1^\circ$ and 66.3°) appeared. The XRD patterns of L95 and L93.8 were nearly the same as that of L100, which indicates no presence of $\text{Li}_4\text{Ti}_5\text{O}_{12}$. This means that L95 and L93.8 are non-stoichiometric compound $\text{Li}_{2-x}\text{TiO}_{3-0.5x}$ and that L90 and L80 are mixtures of $\text{Li}_{2-x}\text{TiO}_{3-0.5x}$ and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. The reaction equation is shown in Table 1.

3.2. Oxygen deficient Li_2TiO_3

The color of L100 and L95 changed from white to dark blue after heating at 1323 K for 10 h under the reducing atmosphere, 20% $\text{H}_2 - 80\%$ Ar ($P_{\text{O}_2} = 5 \times 10^{-24}$ atm) (Fig. 2(b)). This color change indicates that the oxygen content of the sample decreased, suggesting a change from Ti^{4+} to Ti^{3+} . Then, the color of the sample returned to white on oxidation in O_2 gas ($P_{\text{O}_2} = 1 \text{ atm}$) for 10 h, because O atoms entered O-vacancies generated by the earlier reduction. Although the color of L95 became deeper than the color of L100, it is thought that there is a relation with the quantity of the oxygen defects. Similar behavior was confirmed on samples, L90 and L80.

Kleykamp suggested that LiTiO_2 including Ti^{3+} was produced by reduction of a Li_2TiO_3 sample [6]. Therefore, the X-ray diffraction analysis was performed to compare L95, L80 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ kept under the reducing conditions, using a reported pattern of LiTiO_2 [7]. Results of this analysis exhibited that, as shown in Fig. 3, peaks of LiTiO_2 appeared in the X-ray patterns of L80 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ still existed under the reducing condition. But peaks of LiTiO_2 did not appear in the

Table 1
Compositions and reaction equations for Li_2TiO_3 pellets

Notation of sample	Molar ratio $\text{Li}_2\text{O}/\text{TiO}_2$	Reaction equation
L100	1.00	$1.00\text{Li}_2\text{CO}_3 + \text{TiO}_2 \rightarrow \text{Li}_2\text{TiO}_3$
L95	0.95	$0.95\text{Li}_2\text{CO}_3 + \text{TiO}_2 \rightarrow \text{Li}_{1.9}\text{TiO}_{2.95}$
L93.8	0.938	$0.938\text{Li}_2\text{CO}_3 + \text{TiO}_2 \rightarrow \text{Li}_{1.876}\text{TiO}_{2.938}$
L90	0.90	$0.90\text{Li}_2\text{CO}_3 + \text{TiO}_2 \rightarrow 0.929\text{Li}_{1.876}\text{TiO}_{2.938}(\text{L93.8}) + 0.014\text{Li}_4\text{Ti}_5\text{O}_{12}$
L80	0.80	$0.80\text{Li}_2\text{CO}_3 + \text{TiO}_2 \rightarrow 0.744\text{Li}_{1.876}\text{TiO}_{2.938}(\text{L93.8}) + 0.051\text{Li}_4\text{Ti}_5\text{O}_{12}$

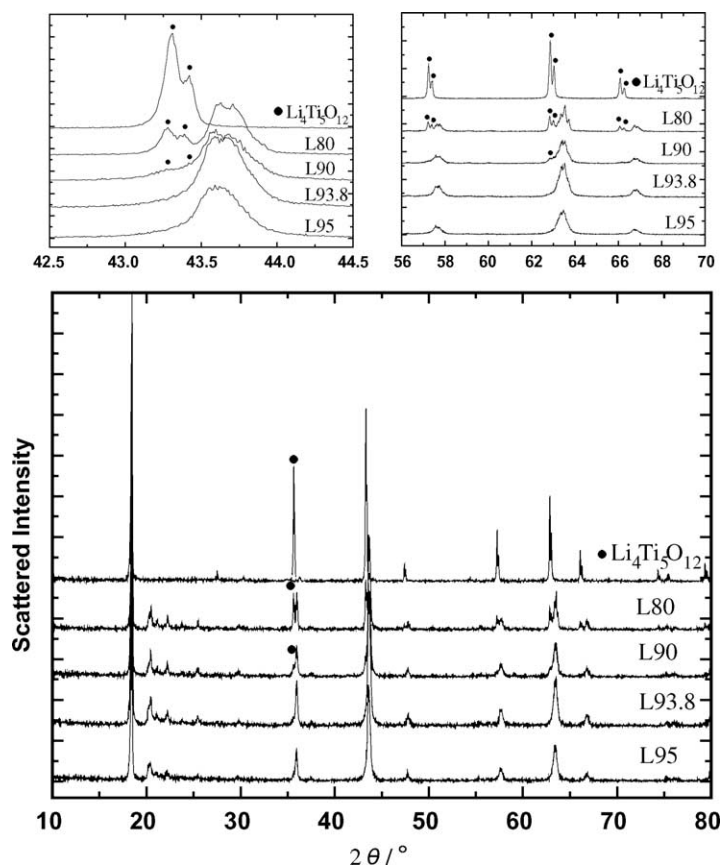


Fig. 1. X-ray diffraction patterns of several Li_2TiO_3 -related compounds.

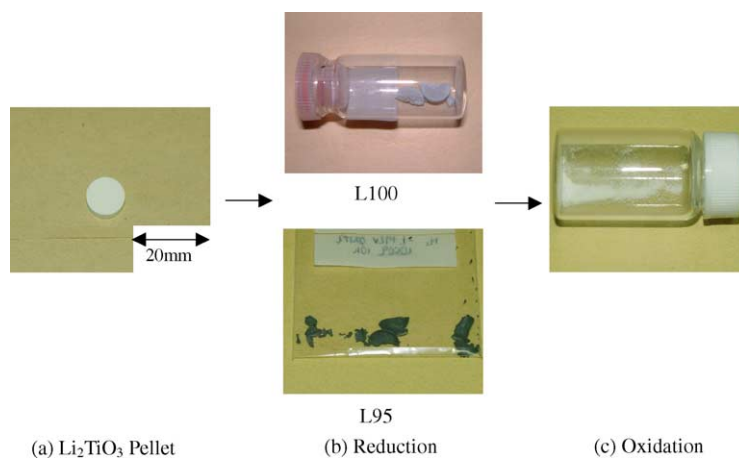


Fig. 2. Sample-color change of L100 and L95 after reduction and oxidation. (For a colour version of this figure see the online paper.)

X-ray pattern of L95. These results suggest that, in case of such a reducing condition, L100 and L95 are not mixtures of $\text{Li}_2\text{TiO}_3 + \text{LiTiO}_2$ but a single phase of a

doubly non-stoichiometric compound, $\text{Li}_{2-x}\text{TiO}_{3-y}$. Moreover, L90 and L80 containing $\text{Li}_4\text{Ti}_5\text{O}_{12}$ are mixtures of $\text{Li}_2\text{TiO}_3 + \text{Li}_4\text{Ti}_5\text{O}_{12} + \text{LiTiO}_2$ in the reduction

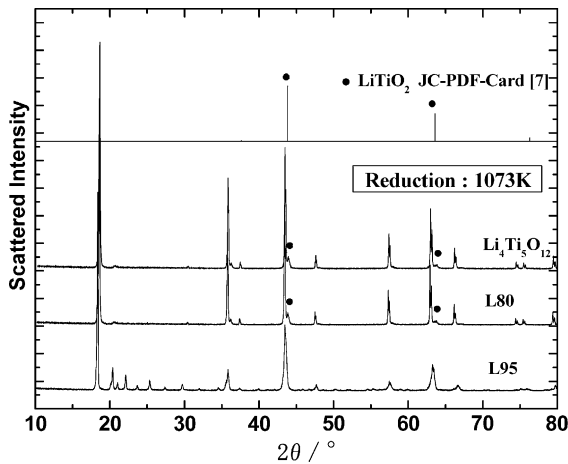


Fig. 3. X-ray diffraction patterns of L95, L80 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ kept in reducing condition as compared to LiTiO_2 .

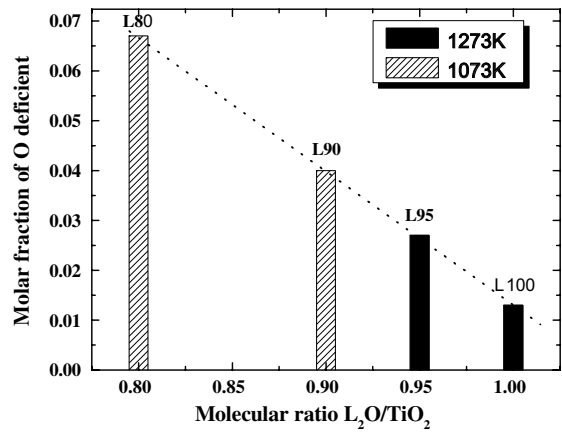


Fig. 4. Molar fraction of O deficiency of several Li_2TiO_3 .

condition. The composition of Li_2TiO_3 in reduction at 1073 K was shown Table 2.

3.3. Measurement of thermogravimetry

For quantitative analysis of non-stoichiometry, the Li_2TiO_3 has been investigated by means of thermogravimetry. The mass of L95 was found to decrease with time in the hydrogen atmosphere, then to increase after the change of the atmosphere from hydrogen to an argon–oxygen mixed gas and then to oxygen [5]. This weight change was similarly seen for other samples, L100, L90 and L80.

The calculation method of molar fraction x of Li_2O deficiency, Li deficiency or O deficiency was described in a previous paper [5]. The calculated result of the molar fraction of oxygen deficiency of Li_2TiO_3 is shown in Fig. 4. The molar fraction of the oxygen deficiency increased as the molecular rate $\text{Li}_2\text{O}/\text{TiO}_2$ decreased with a linear relation between them.

4. Discussion

4.1. Limit of non-stoichiometry

The value of the limit of the molecular ratio was determined from the weight change of L95 in reduction and oxidation by thermogravimetry. Changes in the chemical formula of L95 by reduction and oxidation are shown in Table 2.

The composition of L93.8, Fig. 1 shows that the peak for second phase $\text{Li}_4\text{Ti}_5\text{O}_{12}$, did not appear. The measured value agrees well with the calculated value (Fig. 5), as a result of the molar fraction of oxygen deficiency of L80, which was calculated from the molar fraction of oxygen deficient of L93.8 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$. As a result the limit of the molecular formula was set as $\text{Li}_{1.876}\text{TiO}_{2.938}$ (L93.8).

4.2. Reduction temperature effects

Fig. 4 shows the increase in the molar fraction of oxygen deficiency of Li_2TiO_3 with the decrease in molar ratio $\text{Li}_2\text{O}/\text{TiO}_2$, regardless of temperature. The weight

Table 2
Composition of Li_2TiO_3 in a reduction atmosphere

Sample name	Reaction equation
<i>Reaction equation in reduction at 1073 K</i>	
L100, L95	$\rightarrow \text{Li}_{2-x}\text{TiO}_{3-y}$
L90, L80	$\rightarrow \text{Li}_{1.876}\text{TiO}_{2.938}$ (L93.8) + $\text{Li}_4\text{Ti}_5\text{O}_{12}$ + LiTiO_2
<i>Compositional expressions of L95 after reduction and oxidation</i>	
Pre-measurement molecular formula	$\text{Li}_{1.9}\text{TiO}_{2.95}$ ($\text{Li}_2\text{O}/\text{TiO}_2 = 0.95$)
Molecular formula after reduction	$\text{Li}_{1.876}\text{TiO}_{2.911}$
Molecular formula after oxidation	$\text{Li}_{1.876}\text{TiO}_{2.938}$ ($\text{Li}_2\text{O}/\text{TiO}_2 = 0.938$)

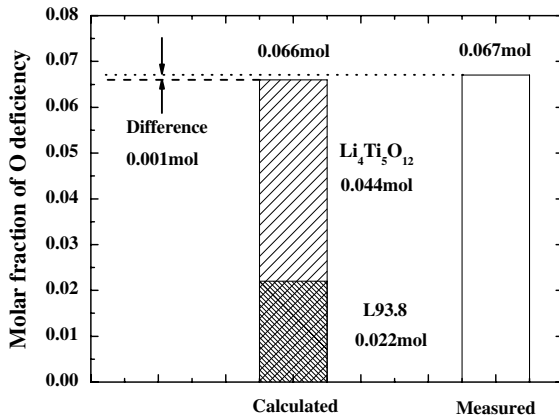


Fig. 5. Comparison between the measured and calculated values of the molar fraction of O deficiency of L80.

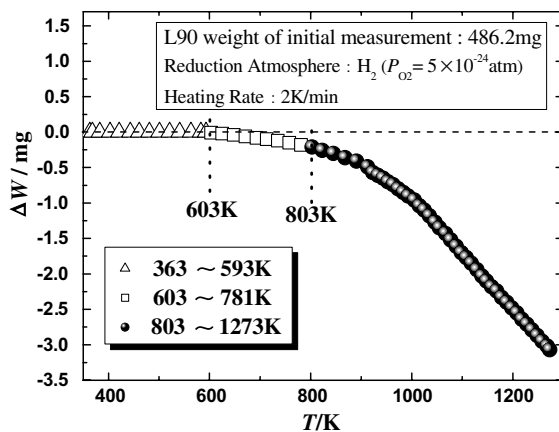


Fig. 6. Temperature dependence of the weight change of L90 in reduction atmosphere observed by thermogravimetry.

change of L90 was measured in the temperature range from room temperature to 1273 K by reduction, in order to investigate the temperature at which reduction occurs. The weight of L90 gradually decreased, generating O-vacancy from about 603 K by reduction, as shown in Fig. 6. Above about 803 K, the weight of L90 decreased quickly with a strong reduction reaction. Therefore, it became clear that there is no influence of temperature on the molar fraction of the oxygen deficiency.

In the present study, there is a lot of hydrogen in the atmosphere and it is a strong reducing atmosphere. However, since there is a report that the color of the sample changes to dark blue, when there is little hydrogen in the atmosphere ($P_{\text{H}_2} = 0.1 - 1.0$ Pa) [8]. Therefore, it is necessary to investigate in detail the

influence of changes in composition on the performance of the breeding blanket.

5. Conclusions

The composition of Li_2TiO_3 has been investigated by means of thermogravimetry, X-ray diffraction and color change observation to examine possible non-stoichiometry.

L100 and L95 indicate both oxygen deficient and also lithium oxide deficient defect formation. Thus, the doubly non-stoichiometric composition, $\text{Li}_{2-x}\text{TiO}_{3-y}$, has been confirmed. On the other hand, L90 and L80 became the mixtures of $\text{Li}_{2-x}\text{TiO}_{3-y}$, $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and LiTiO_2 , and it turned out that LiTiO_2 was generated when the $\text{Li}_4\text{Ti}_5\text{O}_{12}$ phase was exposed to reducing atmospheres.

L80 has more oxygen deficiency than the other kinds of Li_2TiO_3 , and the order of oxygen deficiency was as follows

$$\text{L80} > \text{L90} > \text{L95} > \text{L100}$$

according to the order of the molar ratio $\text{Li}_2\text{O}/\text{TiO}_2$ of the samples. Furthermore the limit of molecular ratio of $\text{Li}_2\text{O}/\text{TiO}_2$ under reduction atmosphere was 0.938, corresponding to the chemical formula $\text{Li}_{1.876}\text{TiO}_{2.938}$ (L98.3).

References

- [1] K. Yamaguchi, A. Suzuki, M. Tonegawa, Y. Takahashi, M. Yasumoto, M. Yamawaki, *J. Mass Spectrom. Soc. Jpn.* 47 (1999) 10.
- [2] N. Roux, J. Avon, A. Floreancig, J. Mougin, B. Rasneur, S. Ravel, *J. Nucl. Mater.* 233–236 (1996) 1431.
- [3] K. Yamaguchi, A. Suzuki, M. Tonegawa, Y. Takahashi, M. Yasumoto, M. Yamawaki, *J. Mass Spectrom. Soc. Jpn.* 47 (1) (1999) 10.
- [4] T. Hoshino, Y. Takahashi, K. Yamaguchi, T. Terai, M. Yamawaki, in: *Proceedings of 9th International Workshop on Ceramic Breeder Blanket Interactions*, 27–29 September 2000 at Toki, Japan, 2000, p. 165.
- [5] T. Hoshino, M. Dokiya, T. Terai, Y. Takahashi, M. Yamawaki, *Fus. Eng. Des.* 353–360 (2002) 61.
- [6] H. Kleykamp, in: *Proceedings of 10th International Workshop on Ceramic Breeder Blanket Interactions*, 22–24 October 2001, Karlsruhe, Germany, 2001.
- [7] PDF#16-0223, PDF-Card, Material Data, *Ann. Chim. Paris*, 1962, p. 513.
- [8] T. Hoshino, M. Yasumoto, Y. Takahashi, T. Terai, M. Yamawaki, *J. Mass Spectrom. Soc. Jpn.* 163–167 (2003) 51.