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Crystal structure of advanced lithium titanate with lithium oxide additives

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ABSTRACT

Li_2TiO_3 is one of the most promising candidates among solid breeder materials proposed for fusion reactors. However, the mass of Li_2TiO_3 was found to decrease with time in the sweep gas mixed with hydrogen. This mass change indicates that the oxygen content of the sample decreased, suggesting the change from Ti^{4+} to Ti^{3+}. In the present paper, the crystal structure and the non-stoichiometry of Li_2TiO_3 added with Li_2O have been extensively investigated by means of X-ray diffraction (XRD) and thermogravimetry. In the case of the Li_2TiO_3 samples used in the present study, $LiO{-}C_2H_5$ or $LiO{-}i{-}C_3H_7$ and $Ti(O{-}i{-}C_3H_7)_4$ were mixed in the proportion corresponding to the molar ratio Li_2O/TiO_2 of either 2.00 or 1.00. In thermogravimetry, the mass of this sample decreased with time due to lithium deficiency, where no presence of oxygen deficiency was indicated.

1. Introduction

Lithium containing ternary oxides ($LiAlO_2$, Li_4SiO_4, Li_2ZrO_3 and Li_2TiO_3) have been proposed as breeder blanket materials [1]. Lithium titanate (Li_2TiO_3) is one of the most promising candidates among the proposed solid breeder materials for fusion reactors because of its high chemical stability, good tritium release and low activation characteristics [2].

Addition of H_2 to inert sweep gas has been proposed for enhancing the release of bred tritium from breeder materials. However, the mass of Li_2TiO_3 was found to decrease with time in the hydrogen atmosphere [3]. This mass change indicates that the oxygen content of the sample decreased, suggesting the change from Ti^{4+} to Ti^{3+}, and also indicates that the partial pressures of Li-containing species were increased in the hydrogen atmosphere. In order to control the mass change at the time of high temperature use, the development of Li_2TiO_3 with Li_2O additive is needed [4]. Furthermore, since Li_2TiO_3 is reduced in hydrogen atmosphere, it is important to investigate the reduction characteristics for the Li_2O addition. In the present paper, the crystal structure and non-stoichiometry of Li_2TiO_3 added with Li_2O have been extensively investigated by means of X-ray diffraction (XRD) and thermogravimetry.

2. Experimental

2.1. Sample

Usually, solid state reaction of Li_2CO_3 and TiO_2 powders is used in the synthesis of Li_2TiO_3. In the present study, however, Li alkoxide ($LiO{-}i{-}C_3H_7$ or $LiO{-}C_2H_5$) and Ti alkoxide ($Ti(O{-}i{-}C_3H_7)_4$) were mixed in C_2H_5OH in order to add Li_2O to Li_2TiO_3. The alkoxide processing steps are shown in Fig. 1 The Li alkoxide and the Ti alkoxide were mixed in the proportion corresponding to the molar ratio Li_2O/TiO_2 of either 1.00 or 2.00. These samples are designated as shown in Table 1. The hydrolysis products were sintered at 1073 K for 8 hr in 5%H_2–He atmosphere. Molar ratio Li_2O/TiO_2 of the samples was evaluated by Inductively Coupled Plasma atomic emission spectrometry (ICP).

2.2. X-ray diffraction analysis

In order to examine the crystal structure, the Li_2TiO_3 samples were examined by using XRD technique. Powder X-ray diffraction patterns were obtained using a beam of CuKα radiation ($\lambda = 1.5418$ Å) generated with RINT2000 of Rigaku Co. The operational settings for all the X-ray diffraction scans were as follows;

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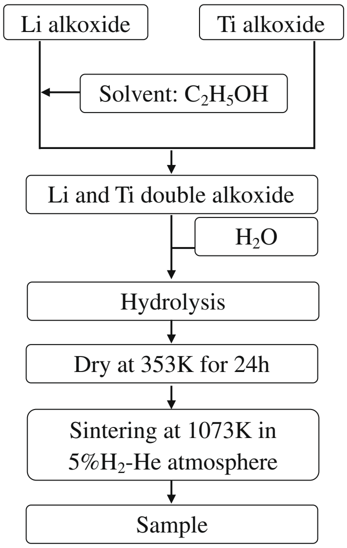


Fig. 1. Flow sheet of alkoxide processing steps.

voltage: 50 kV, current: 250 mA, 2θ range: 10–80 °; scanning speed: 6.0 °min^{-1} and slit width: 0.02 °.

2.3. Thermogravimetry

The apparatus used was a thermogravimetry Model Cahn-2000 of Cahn Instruments, Inc., USA. The weight changes were measured with an accuracy of ±0.01 mg for 0.3–0.5 g samples. Different oxygen partial pressures were maintained by using 5% H_2–He(reducing atmosphere)/He(oxidizing atmosphere)/O_2(oxidizing atmosphere) system with the flow rates around 60 cm^3/min. Changes in stoichiometry were studied at 1173 K.

3. Results and discussion

3.1. Hydrolysis of alkoxide

Before hydrolysis, the solution of EPL200 was colorless and transparent (Fig. 2). On the other hand, PPL100 and PPL200 were white cloudy solution, because LiO–i–C_3H_7 did not completely dissolve into the solvent. After hydrolysis, white gel was dried and sintered at 1073 K for 8 hr in 5%H_2–He atmosphere.

The color of the samples of PPL200 and EPL200 was white, and that of PPL100 was dark blue. This dark blue color suggests the valency change from Ti^{4+} to Ti^{3+}, which should have been accompanied by the decrease in the oxygen content of the sample, because the color was observed to change from dark blue to white under the oxygen atmosphere (Fig. 3).

The molar ratios for the reaction products of PPL100 and EPL200 obtained by ICP were almost in agreement with the value for the starting materials of the alkoxides mixed (Table 1). It is considered that the reason for the lower molar ratio for the reaction product of PPL200 than the value at mixture is that LiO–i–C_3H_7 did not completely dissolve into the solvent.

3.2. Structural characteristics

Li_2TiO_3 is a non-stoichiometric compound $Li_{2\pm x}TiO_{3\pm x}$ as modeled by Kleykamp [4–5]. In order to examine this model, SSL100, PPL100, PPL200 and EPL200 were analyzed by XRD technique. The results of the XRD analysis are shown in Fig. 4. The XRD patterns of SSL100 and PPL100 were almost the same as that of Li_2TiO_3 listed in JC-PDF-Card [6], where no presence of Li_4TiO_4 was

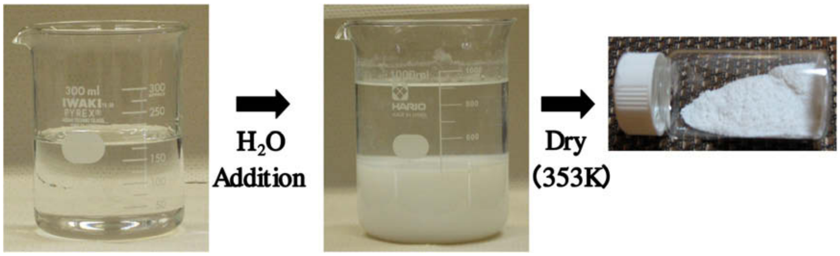
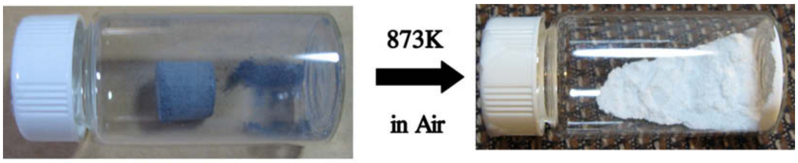


Fig. 2. Hydrolysis of EPL200.



(a) PPL100

(b) PPL200

(c) EPL200

Fig. 3. Color of PPL100, PPL200 and EPL200 after being sintered at 800 °C in 5%H_2–He atmosphere.

Table 1
Reaction products and molar ratio of samples SSL100, PPL100, PPL200 and EPL200.

Notation of Sample	Starting Materials		Molar ratio Li_2O/TiO_2	Reaction	Reaction Product	Molar ratio Li_2O/TiO_2 [Measurements by ICP]
	Li	Ti				
SSL100	Li_2CO_3	TiO_2	1.00	Solid State Reaction	Li_2TiO_3	1.00
PPL100	$LiO{-}i{-}C_3H_7$	$Ti(O{-}i{-}C_3H_7)_4$	1.00	Hydrolysis of Alkoxide	$Li_{1.97}TiO_{2.985}$	0.985
PPL200	$LiO{-}i{-}C_3H_7$	$Ti(O{-}i{-}C_3H_7)_4$	2.00	Hydrolysis of Alkoxide	$Li_{2+x}TiO_{3+y}$ + small amount Li_4TiO_4	1.21
EPL200	$LiO\text{-}C_2H_5$	$Ti(O{-}i{-}C_3H_7)_4$	2.00	Hydrolysis of Alkoxide	$Li_{2+x}TiO_{3+y}$ + Li_4TiO_4	1.97

indicated. In contrast, the XRD pattern of PPL200 showed small peaks of Li_4TiO_4 [7]. Furthermore, it was revealed from the XRD pattern that EPL200 is a mixture of the non-stoichiometric compound $Li_{2+y}TiO_{3+y}$ and Li_4TiO_4.

Lattice parameters of PPL100, PPL200 and EPL200 were evaluated from the XRD data (Fig. 5). It was found that the Li_2O/TiO_2 dependence of the lattice parameters showed no change for all the samples. This result suggests that excess Li in PPL200 and EPL200 exists as interstitial atom of Li_2TiO_3.

3.3. Molar fraction of O deficiency

For quantitative analysis of non-stoichiometry at 1123 K, the samples were investigated by means of thermogravimetry. The mass of PPL200 was found to decrease with time in the hydrogen atmosphere, and then it increased a little after the change of the atmosphere from hydrogen to helium–oxygen gas mixture and

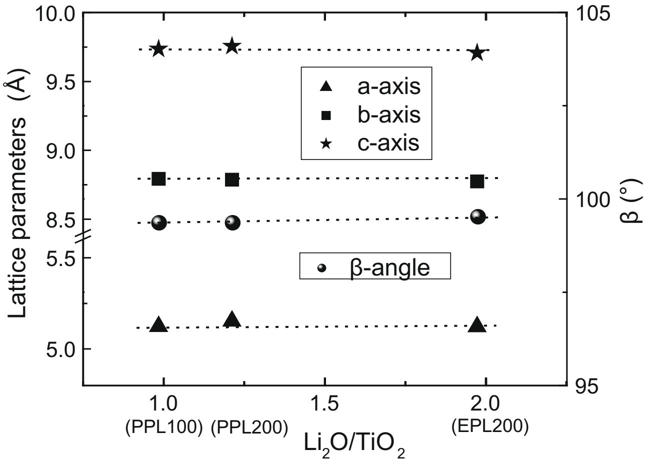
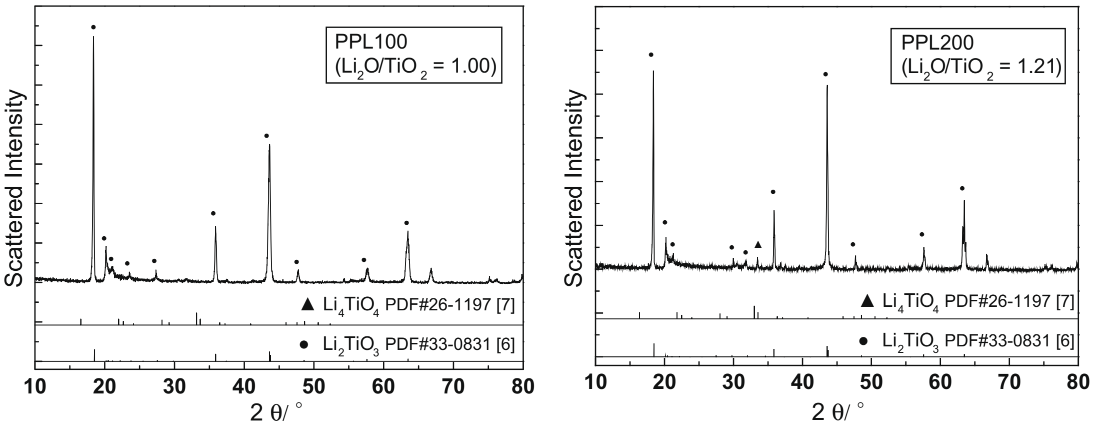
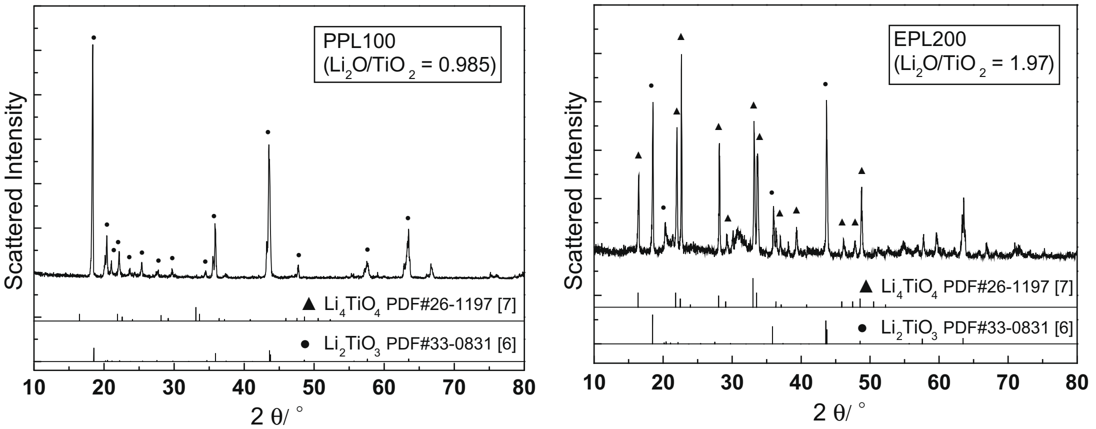


Fig. 5. Lattice parameters of PPL100, PPL200 and EPL200.



(a) SSL100

(c) PPL200



(b) PPL100

(d) EPL200

Fig. 4. X-ray diffraction patterns of samples SSL100, PPL100, PPL200 and SSL200 as compared to those in JC-PDF-Card [6–7].

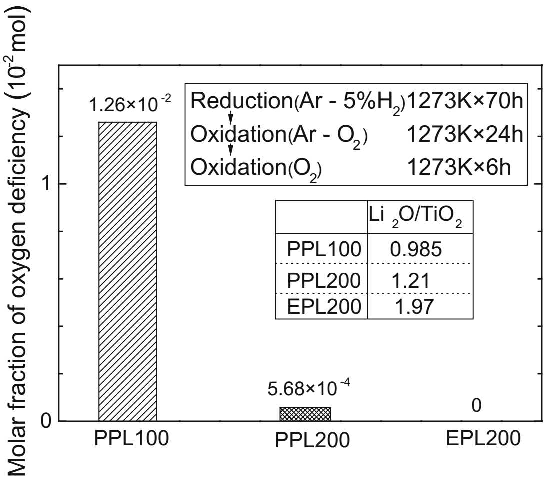


Fig. 6. Molar fraction of oxygen deficiency of PPL100, PPL200 and EPL200.

then to oxygen. In the case of the reduction atmosphere, the detected vapor species were Li, LiOH, Li_2O and LiO [8]. Therefore, the Li_2O weight loss as much as 8.32 mg is attributed to vaporization, while oxygen deficient of 0.04 mg to a valency change from Ti^{4+} to Ti^{3+} caused by reduction. Similar weight change was observed for PPL100 and EPL200.

Molar fraction x of oxygen deficient was calculated using Eq. (1),

$$x(mol) = \frac{\Delta \mathbf{W} \cdot \mathbf{M}}{\mathbf{W}_0 \mathbf{X}_{\mathrm{mol}}}, \tag{1}$$

where ΔW: weight variance, *M*: molecular weight of the sample, W_0: weight of the sample before reduction, and X_{mol}: molecular weight of oxygen. The calculation result of the molar fractions of oxygen deficient of PPL100, PPL200 and EPL200 are shown in Fig. 6. The molar fraction of oxygen deficient decreased as the molar ratio Li_2O/TiO_2 increased. The result of EPL200 indicated no presence of oxygen defects as compared with the other kinds of samples; this probably reflects the much smaller mass of TiO_2 for EPL200 in $Li_2TiO_3 + Li_4TiO_4$ than that for PPL100 and PPL200. It was proved that Li_2TiO_3 becomes difficult to be reduced by lithium oxide additives.

4. Conclusions

In order to control the mass change at the time of high temperature use, the development of Li_2TiO_3 with Li_2O additive was attempted using Li alkoxide (LiO–i–C_3H_7 or LiO–C_2H_5) and Ti alkoxide (Ti(O–i–C_3H_7)$_4$), and then the crystal structure and the non-stoichiometry of the Li_2TiO_3 added with Li_2O have been extensively investigated by means of XRD and thermogravimetry.

The XRD measurement showed that the diffraction pattern of sample EPL200 was almost the same as that of a mixture of Li_2TiO_3 and Li_4TiO_4. This indicates that PPL200 is a non-stoichiometric compound $Li_{2+x}TiO_{3+y} + Li_4TiO_4$.

In thermogravimetry, the masses of the samples were found to decrease with time in the hydrogen atmosphere, which was partly due to the generation of oxygen defects of the samples. The molar fraction of the oxygen defects increased as the molar ratio Li_2O/TiO_2 decreased, and EPL200 did not have oxygen defects as compared with the other kinds of samples.

The overall results indicate that the Li_2O addition is effective in controlling the amount of oxygen defects. Thus, the present study confirmed the validity of Li_2O addition to Li_2TiO_3 for developing high temperature resistant breeding materials using the alkoxide reaction.

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