

# Phase equilibria in the Li–Ti–O system and physical properties of $\text{Li}_2\text{TiO}_3$

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## Abstract

The phase equilibria of the pseudo-binary  $\text{Li}_2\text{O}$ – $\text{TiO}_2$  system and the stoichiometry shift of  $\text{Li}_2\text{TiO}_3$  during the Li transmutation process are investigated. The structural properties, the thermal expansion, enthalpy, heat capacity, enthalpy of transformation and melting, thermal conductivity and the vapourisation behaviour of  $\text{Li}_2\text{TiO}_3$  are assessed. The ternary Li–Ti–O system is treated with emphasis to the characteristic of  $\text{Li}_2\text{TiO}_3$  under reducing conditions. The phase is reduced to  $\text{LiTiO}_2$  with the Ti valence +3 due to its transition metal character.

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**Keywords:** Phase equilibria; Li–Ti–O system; Thermal properties

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## 1. Introduction

Lithium-based oxide ceramics are being considered as possible solid breeder materials in the blanket of future fusion reactors. The role of the breeder material is to produce tritium atoms by lithium transmutation. As the heat generated by the nuclear reaction is absorbed also by the blanket and is transported to the coolant, the structural, thermal and transport properties of breeder materials are important for the design of a blanket system. Short-listed candidates are  $\text{Li}_4\text{SiO}_4$ ,  $\text{Li}_2\text{TiO}_3$  and  $\text{Li}_2\text{ZrO}_3$  which change their composition (Li/M atomic ratio) during the lithium transmutation and beyond that their

stoichiometry ( $\text{O}/(\text{Li}+\text{M})$  atomic ratio) under reducing operation conditions. These characteristic features are elucidated by phase equilibria studies in the respective pseudo-binary and ternary systems.

Lithium metatitanate of the composition  $\text{Li}_2\text{TiO}_3$  ( $M = 109.76$ ) attracted more recently higher attention by its promising tritium release rates at low temperatures between 200 and 400 °C [1–3]. Therefore, phase equilibria studies in the Li–Ti–O system and physical property measurements on  $\text{Li}_2\text{TiO}_3$  were summarised in this article with emphasis to the results of this laboratory.

## 2. The pseudo-binary $\text{LiO}_2$ – $\text{TiO}_2$ system

The system is characterised by four ternary oxides:  $\text{Li}_4\text{TiO}_4$ ,  $\text{Li}_2\text{TiO}_3$  in three modifications,  $\text{Li}_4\text{Ti}_5\text{O}_{12}$ , and the high-temperature phase  $\text{Li}_2$ –

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$\text{Ti}_3\text{O}_7$  which decomposes eutectoidally at about 950 °C [4,5]. The  $\beta$ -modification of  $\text{Li}_2\text{TiO}_3$  has a narrow homogeneity range between 47 and 51 mol%  $\text{TiO}_2$  [4] and 52 mol%  $\text{TiO}_2$  [5], respectively. The large homogeneity range of the  $\gamma$ -modification extends across about 42–66 mol%  $\text{TiO}_2$  [4]. In order to ensure small grains during fabrication and to limit grain growth during operation a lithium deficiency with reference to the stoichiometric composition,  $\text{Li}_{1.9}\text{TiO}_{3-x}$ , is intended for the use as breeding material. This composition is located near the  $\text{TiO}_2$ -rich phase boundary of  $\beta$ - $\text{Li}_2\text{TiO}_3$ . [1,2]. As a consequence of the Li transmutation process, the oxide becomes two-phase, and  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  below 930 °C and  $\gamma$ - $\text{Li}_2\text{TiO}_3$  above 930 °C are formed as the second phases [7]. The enantiotropic  $\beta$ - $\gamma$  (m-c) transformation of stoichiometric  $\text{Li}_2\text{TiO}_3$  is reported at 1215 °C [4],

1212 °C [8], 1155 °C, extrapolated [6], and 1150 °C [5,10], that of  $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$  near the  $\text{TiO}_2$  rich phase boundary at 1137 °C [6]; this temperature is the  $\beta$  to  $\beta+\gamma$  phase boundary transition. A  $\beta$ - $\gamma$  transformation at 1170 °C was reported for the composition  $\text{Li}_{1.9}\text{TiO}_{3-x}$  [9]. The  $\gamma$ -modification melts congruently at 1547 °C [8] and 1535 °C [5,10], respectively.

The re-investigation of the  $\text{Li}_2\text{O}$ - $\text{TiO}_2$  system within the  $\text{Li}_2\text{TiO}_3$  range by DTA in Pt crucibles yields:  $\beta$ - $\gamma$  transition temperature  $T_{\text{tr}} = (1155 \pm 3)$  °C, melting temperature  $T_{\text{m}} = (1533 \pm 5)$  °C (stoichiometric composition); homogeneity ranges at the  $\text{TiO}_2$  rich phase boundary:  $\beta$ - $\text{Li}_2\text{TiO}_3$  at 51.5 at.%  $\text{TiO}_2$ ,  $\gamma$ - $\text{Li}_2\text{TiO}_3$  up to 60 at.%  $\text{TiO}_2$ ; eutectic formation: liquid = c- $\text{Li}_2\text{TiO}_3$  +  $\text{Li}_2\text{Ti}_3\text{O}_7$  at 1291 °C / 74 at.%  $\text{TiO}_2$ ; peritectoid formation: c- $\text{Li}_2\text{TiO}_3$  +  $\text{Li}_2\text{Ti}_3\text{O}_7$  =  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 1018 °C / 71.4 at.%  $\text{TiO}_2$ ; eutectoid formation: c- $\text{Li}_2\text{TiO}_3$  = m- $\text{Li}_2\text{TiO}_3$  +  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  at 930 °C / 58 at.%  $\text{TiO}_2$ . The results are graphically presented in Fig. 1.

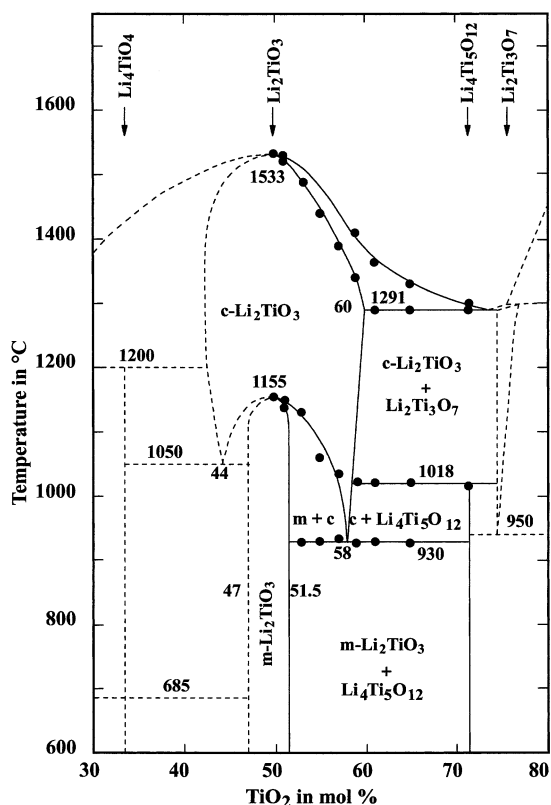


Fig. 1. Phase diagram of the  $\text{Li}_2\text{O}$ - $\text{TiO}_2$  system; broken lines: from Izquierdo and West [4] and from Mikkelsen [5]; solid lines: this work.

### 3. Structural properties

The phase  $\text{Li}_2\text{TiO}_3$  exists in three modifications,  $\alpha$ ,  $\beta$  and  $\gamma$  [4,5]. The  $\alpha$ -phase is metastable and has a monotropic transformation to  $\beta$ - $\text{Li}_2\text{TiO}_3$  by heating above 300 °C [10]. First heating of  $\text{Li}_2\text{TiO}_3$  prepared by arc-melting results in an endothermic irreversible DTA signal at 960 °C, which is assigned to the monotropic  $\alpha$ - $\beta$  transformation [7]. The low-temperature  $\beta$ -phase is monoclinic, has a narrow homogeneity range and crystallises in the  $\text{Li}_2\text{SnO}_3$ -type structure with the space group  $\text{C2/c}$  (No. 15),  $Z = 8$ , and the lattice parameters  $a = 504.1$  pm,  $b = 880.6$  pm,  $c = 972.7$  pm and  $\beta = 100.0^\circ$ . The room temperature (RT) X-ray density is  $\rho_x = 3.43$  Mg/m<sup>3</sup> [11]. The high-temperature  $\gamma$ - $\text{Li}_2\text{TiO}_3$  is cubic and crystallises in the NaCl-type structure,  $Z = 4/3$ , with the RT lattice parameter  $a = 415.05$  pm. The RT X-ray density is  $\rho_x = 3.40$  Mg/m<sup>3</sup> [11]. The RT lattice parameters of the  $\beta$ -phase annealed in dry air at 900 °C were further measured near its  $\text{TiO}_2$ -rich phase boundary with 48.2 mol%  $\text{Li}_2\text{O}$ , 51.3 mol%  $\text{TiO}_2$  and 0.5 mol% other oxides (as a result of the chemical analysis) which corresponds to the nor-

malised formula  $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$ , and give  $a = (505.4 \pm 0.5)$  pm,  $b = (877.9 \pm 0.7)$  pm,  $c = (975.7 \pm 1.1)$  pm and  $\beta = (100.1 \pm 0.1)^\circ$  [6].

#### 4. Linear thermal expansion

An early result of the linear thermal expansion of  $\text{Li}_2\text{TiO}_3$  between  $t = 100$  and  $800^\circ\text{C}$  determined by an unknown method is given by  $\Delta l/l_0 = -5.573 \times 10^{-4} + 1.455 \times 10^{-5}t + 5.505 \times 10^{-9}t^2$  [12]. The linear thermal expansion coefficient  $\alpha$  can be calculated therefrom. The linear thermal expansion of  $\text{Li}_{1.9}\text{TiO}_{3-x}$  was measured further by dilatometry up to  $800^\circ\text{C}$ . Average linear thermal expansion coefficients were reported:  $\bar{\alpha} = 20.5 \times 10^{-6} \text{ K}^{-1}$  ( $300\text{--}500^\circ\text{C}$ ),  $\bar{\alpha} = 21.5 \times 10^{-6} \text{ K}^{-1}$  ( $500\text{--}700^\circ\text{C}$ ) [9]. Other linear thermal expansion data on  $\text{Li}_2\text{TiO}_3$  by laser interferometry up to  $700^\circ\text{C}$  are given in Ref. [13]. Results are shown in Fig. 2. The lattice parameters of  $\beta$ - and  $\gamma$ - $\text{Li}_2\text{TiO}_3$

Table 1

Lattice parameters of monoclinic  $\beta$ - $\text{Li}_2\text{TiO}_3$  and cubic  $\gamma$ - $\text{Li}_2\text{TiO}_3$  as a function of temperature. Monoclinic angle  $\beta = 100.2^\circ$  [14]. Exact composition: 95 mol%  $\text{Li}_2\text{TiO}_3$ –5 mol%  $\text{TiO}_2$  ( $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$ )

| $t$ ( $^\circ\text{C}$ ) | $a$ (pm) | $b$ (pm) | $c$ (pm) |
|--------------------------|----------|----------|----------|
| 25                       | 504.88   | 879.16   | 977.12   |
| 300                      | 506.23   | 878.51   | 976.93   |
| 400                      | 507.27   | 878.76   | 976.58   |
| 500                      | 507.37   | 880.21   | 977.13   |
| 600                      | 509.34   | 880.94   | 977.12   |
| 700                      | 509.03   | 881.62   | 977.85   |
| 800                      | 509.88   | 885.52   | 984.58   |
| 900                      | 513.64   | 888.48   | 989.21   |
| 1000                     | 514.83   | 891.49   | 992.69   |
| 1050                     | 514.53   | 893.93   | 995.10   |
| 25 <sup>a</sup>          | 415.1    | –        | –        |
| 1000 <sup>b</sup>        | 422.6    | –        | –        |
| 1125                     | 423.6    | –        | –        |
| 1250                     | 425.1    | –        | –        |

<sup>a</sup> Extrapolated.

<sup>b</sup> During cooling.

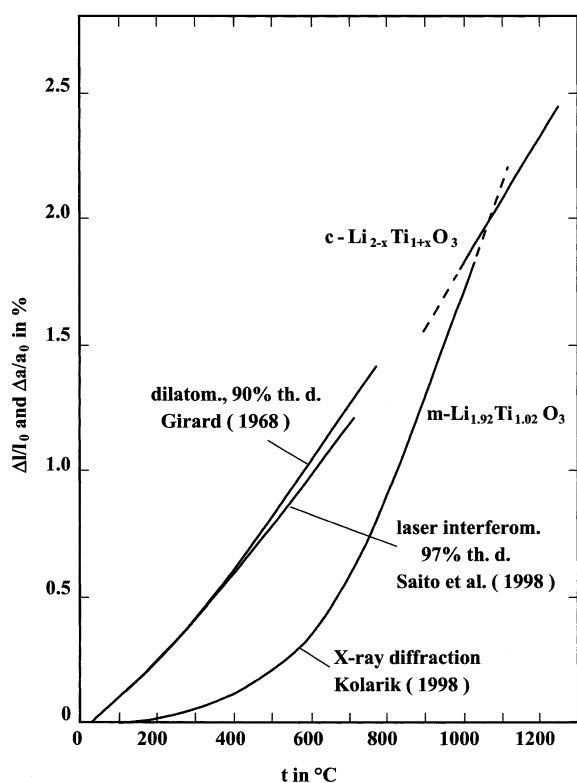


Fig. 2. Linear thermal expansion  $\Delta l/l_0$  of  $\text{Li}_2\text{TiO}_3$ .

with the composition 95 mol%  $\text{Li}_2\text{TiO}_3$ –5 mol%  $\text{TiO}_2$  were measured by high-temperature X-ray diffraction (Table 1) [14]. The quasi-isotropic linear thermal expansion  $\Delta l/l_0 = \frac{1}{3}\Delta V/V_0$  with  $V = abc \sin \beta$  is presented in Fig. 2. The temperature dependence of the fitted curve is approximately parabolic up to  $700^\circ\text{C}$ , which is followed by an almost linear behaviour at higher temperatures. Analytical equations of the linear thermal expansion coefficient are  $\alpha = 1.28 \times 10^{-6} - 1.56 \times 10^{-8}t + 7.48 \times 10^{-11}t^2$ ,  $t = 20\text{--}700^\circ\text{C}$ , and  $\alpha = 8.3 \times 10^{-6} + 2.7 \times 10^{-8}t$ ,  $t = 700\text{--}1000^\circ\text{C}$ ,  $\alpha$  in  $\text{K}^{-1}$ .

#### 5. Enthalpy and heat capacity

The enthalpy of stoichiometric  $\text{Li}_2\text{TiO}_3$  was measured by drop calorimetry between 388 and  $1856 \text{ K}$  [8]. The heat capacity of stoichiometric  $\beta$ - $\text{Li}_2\text{TiO}_3$  was determined by the laser flash method up to  $1000 \text{ K}$  [15], by differential scanning calorimetry (DSC) up to  $1100 \text{ K}$  [13] and on non-stoichiometric material with  $\text{Li/Ti} = 1.9$  by DSC up to  $1000 \text{ K}$  [1,9]. The enthalpy of  $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$  was further measured by drop ca-

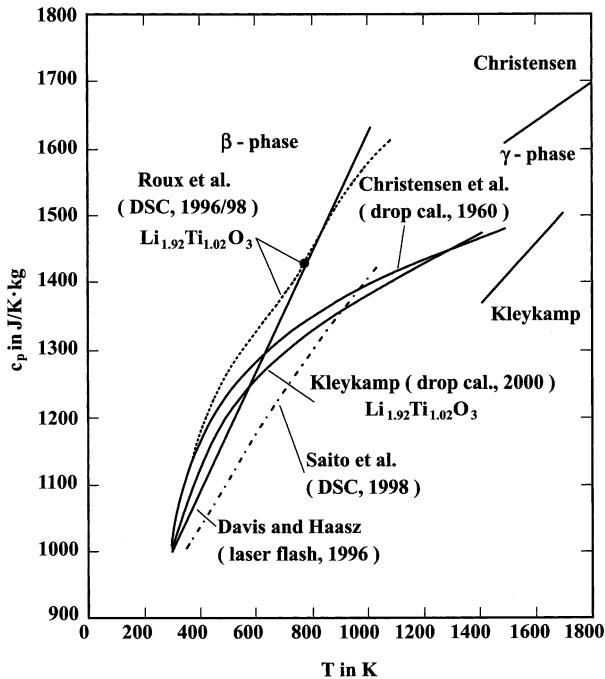


Fig. 3. Specific heat capacity  $c_p$  of  $\text{Li}_2\text{TiO}_3$ .

lorimetry between 397 and 1650 K which gives  $H^\circ(T) - H^\circ(298 \text{ K}) = -49181 + 131.876T + 0.011097T^2 + 2651112T^{-1} \text{ J/mol}$  (298–1410 K) for the monoclinic phase and  $H^\circ(T) - H^\circ(298 \text{ K}) = +49729 + 50.517T + 0.031679T^2 - 20143786T^{-1} \text{ J/mol}$  (1410–1700 K) for the cubic phase. The heat capacity of the phases was evaluated by differentiation. The value extrapolated to 298 K is  $C_p(298 \text{ K}) = (108.6 \pm 2.5) \text{ J/K mol}$  [6]. An early result of  $C_p(298 \text{ K}) = 111.0 \text{ J/K mol}$  was reported in Ref. [8]. The specific heat capacity  $c_p$  of  $\text{Li}_2\text{TiO}_3$  as a function of temperature is presented in Fig. 3.

## 6. Enthalpy of transformation and melting

The enthalpy of the  $\beta$ – $\gamma$  transformation and melting of  $\text{Li}_2\text{TiO}_3$  was evaluated from the enthalpy measurements of the modifications by drop calorimetry resulting in  $\Delta_{tr}H = 11.5 \text{ kJ/mol}$  and  $\Delta_mH = 110 \text{ kJ/mol}$  [8]. The enthalpy of transformation of  $\text{Li}_2\text{TiO}_3$  near its  $\text{TiO}_2$ -rich boundary (51.3 mol%  $\text{TiO}_2$ ) resulted from the enthalpies of

the modifications at the interpolated transformation temperature in  $\Delta_{tr}H = 8950 \text{ J/mol}$  and directly by anisothermal calorimetry in  $\Delta_{tr}H = 9390 \text{ J/mol}$ . This gives an average value  $\Delta_{tr}H = (9200 \pm 300) \text{ J/mol}$  [6].

## 7. Thermal conductivity

The thermal diffusivity of  $\text{Li}_2\text{TiO}_3$  with 81.4% theoretical density (th.d.) was measured by the laser flash method between 200 and 1100 °C. The thermal conductivity calculated therefrom ranges between 1.7 and 2.1 W/K m [3,16]. Similar experiments on  $\text{Li}_2\text{TiO}_3$  with 86.6% th.d. were made between RT and 720 °C. The thermal conductivity ranges between 3 and 2.2 W/K m [15]. Further data by the same method are available on material with th.d. between 73 and 93% in the temperature range RT–800 °C. Thermal conductivity data therefrom were obtained between 2.6 and 1.6 W/K m [13]. The thermal diffusivity was further

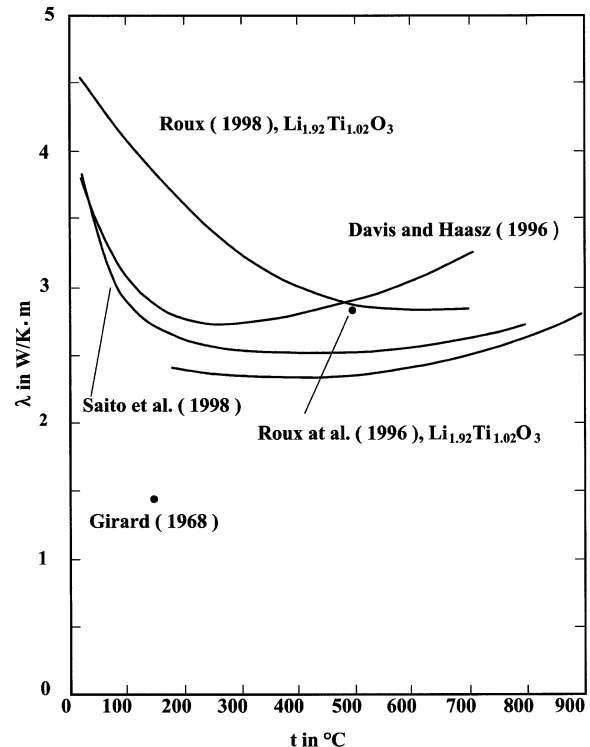


Fig. 4. Thermal conductivity  $\lambda_0$  of 100% th.d.  $\text{Li}_2\text{TiO}_3$ .

measured on non-stoichiometric  $\text{Li}_{1.9}\text{TiO}_{3-x}$  with 87% th.d. between RT and 700 °C. The thermal conductivity is possibly slightly higher and decreases from 3.5 to 2.3 W/K m with increasing temperature [9]. Further data are shown in Ref. [1].

All thermal conductivity data  $\lambda_P$  of porosity  $P$  were converted into the data  $\lambda_0$  of 100% th.d. ( $P = 0$ ) using the formula  $\lambda_P = \lambda_0(1-P)^{3/2}$  developed by Schulz for spherical pores on a physical basis [17]. The non-linearity can be evidenced by a Taylor series development  $\lambda_P = \lambda_0(1 - (3/2)x + (3/8)x^2 - \dots)$ . The results of  $\text{Li}_2\text{TiO}_3$  with 100% th.d. are presented in Fig. 4. A recommendation is given by  $\lambda_0 = (2.7 \pm 0.3)$  W/K m between 100 and 900 °C.

## 8. Vapourisation

The vapourisation of  $\text{Li}_2\text{TiO}_3$  has been investigated by the mass spectrometric Knudsen effusion method under vacuum between 1180 and 1630 K. The species with the highest partial pressure is Li, followed by  $\text{Li}_2\text{O}$ , LiO and  $\text{O}_2$  [18,19]. Further measurements were made between 1370 and 1680 K under reducing and oxidising conditions using  $\text{D}_2$  and  $\text{D}_2\text{O}$  vapour, respectively, of about  $5 \times 10^{-6}$  bar [20]. The partial pressures above  $\text{Li}_2\text{TiO}_3$  at 1500 K are presented in Table 2. The Li pressure is enhanced under  $\text{D}_2$  atmosphere, LiOD and  $\text{D}_2\text{O}$  are formed, the partial pressure of the latter increases with decreasing temperature. The Li pressure is only slightly influenced under  $\text{D}_2\text{O}$  atmosphere, however, the  $\text{D}_2\text{O}$  pressure rises with decreasing temperature by enhanced decomposition of LiOD at lower temperatures.

Table 2

Partial pressures above solid  $\text{Li}_2\text{TiO}_3$  under vacuum and under deuterium and heavy water atmospheres at 1500 K [18–20]

| Atmosphere                                          | Species in bar       |                       |                     |                      |                    |                    |
|-----------------------------------------------------|----------------------|-----------------------|---------------------|----------------------|--------------------|--------------------|
|                                                     | Li                   | $\text{Li}_2\text{O}$ | LiO                 | $\text{D}_2\text{O}$ | LiOD               | $\text{D}_2$       |
| Vacuum                                              | $1.0 \times 10^{-6}$ | $4 \times 10^{-9}$    | $1 \times 10^{-9}$  | –                    | –                  | –                  |
| $\approx 5 \times 10^{-6}$ bar $\text{D}_2$         | $3.0 \times 10^{-6}$ | $8 \times 10^{-9}$    | $2 \times 10^{-9}$  | $5 \times 10^{-6}$   | $2 \times 10^{-6}$ | –                  |
| $\approx 5 \times 10^{-6}$ bar $\text{D}_2\text{O}$ | $1.1 \times 10^{-6}$ | $2 \times 10^{-9}$    | $9 \times 10^{-10}$ | –                    | $2 \times 10^{-6}$ | $2 \times 10^{-7}$ |

## 9. The Li–Ti–O system

Systematic constitutional work in the ternary Li–Ti–O system has not yet been done. However, an isothermal section of the oxygen rich part is sketched at 900 °C and 1 bar total pressure in Fig. 5, which is based on information from the literature [11,21–23] and on own work [7].  $\text{Li}_4\text{Ti}_5\text{O}_{12}$  and  $\text{Li}_4\text{Ti}_{11}\text{O}_{20}$  are the end members of the solid solution. The phase field distribution in the Ti oxide rich area is incomplete. Annealing of  $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$  at 900 °C under purified argon (that has swept over hot zirconium sponges ( $p(\text{O}_2) = 10^{-39}$  bar) resulted in a second phase which was identified as cubic  $\text{LiTiO}_2$  by Guinier method X-ray diffraction [7]. The remaining  $\text{Li}_{1.92}\text{Ti}_{1.02}\text{O}_3$  phase has under reducing conditions lattice parameters very similar to those under oxidising

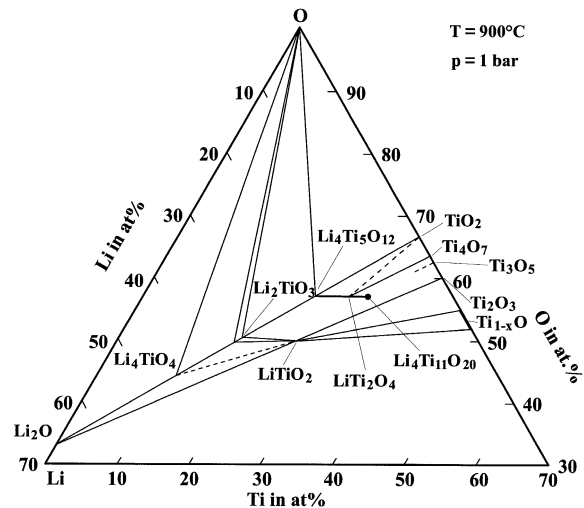


Fig. 5. Tentative isothermal section of the Li–Ti–O system at 900 °C and 1 bar total pressure.

conditions. This gives no evidence of a homogeneity range in the metal–oxygen direction of the Li–Ti–O system. Long-term annealing of  $\text{Li}_2\text{TiO}_3$  pellets at 970 °C for 96 d under He-0.1 vol.%  $\text{H}_2$  atmosphere and 1 bar total pressure led to precipitates in the surface region and on inner grain boundaries which were identified as  $\text{LiTiO}_2$  with the RT lattice parameter  $a = (414.4 \pm 0.2)$  pm [7] possibly according to the reaction  $6\text{Li}_2\text{TiO}_3 = 4\text{LiTiO}_2 + 2\text{Li}_4\text{TiO}_4 + \text{O}_2$ . This means a mass loss of the solid solely by the reduction process. The released oxygen oxidises tritium, which is formed by lithium transmutation during  $\text{Li}_2\text{TiO}_3$  irradiation. The observation implies a change of the Ti valence to the +3 state under reducing conditions due to its multi-valent transition metal character. The formation of the second phase could influence the tritium release behaviour of irradiated  $\text{Li}_2\text{TiO}_3$ .

## 10. Summary

Monoclinic  $\text{Li}_2\text{TiO}_3$  has a narrow homogeneity range. The use of the oxide at the  $\text{TiO}_2$  rich phase boundary is proposed as breeding material in order to optimise the grain size and consequently, the tritium release during irradiation. The application of the material under a reducing atmosphere results in part in the formation of  $\text{LiTiO}_2$  by change of the four-valence to the three-valence state of the transition metal titanium. The discussed physical properties were accurately determined with the exception of the very structure-sensitive heat conductivity where an uncertainty remains.

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