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Enthalpy, heat capacity and enthalpy of transformation of Li_2TiO_3

Heiko Kleykamp *

Forschungszentrum Karlsruhe, Institut für Materialforschung I, Postfach 3640, 76021 Karlsruhe, Germany

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Abstract

The enthalpy of β- and γ-Li_2TiO_3 (Li/Ti = 1.88) was measured between 397 and 1650 K by isothermal drop calorimetry. The smoothed enthalpy curve between 298 and 1700 K results in $H°(T) - H°(298\ \mathrm{K}) = -49181 + 131.876T + 0.011097T^2 + 2651112T^{-1}$ J/mol (298–1410 K) and $H°(T) - H°(298\ \mathrm{K}) = +49729 + 50.517T + 0.031679T^2 - 20\,143\,786T^{-1}$ J/mol (1410–1700 K). The heat capacity was derived by differentiation of the enthalpy curve. The value extrapolated to 298 K is $C_{p,298} = (108.6 \pm 2.5)$ J/K mol. The enthalpy of the monoclinic–cubic transformation of Li_2TiO_3 was determined by anisothermal calorimetry and gives $\Delta_{tr}H = (9200 \pm 300)$ J/mol at about 1410 K.

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 from lithium transmutation which then act as fuel components of the reactor. As the heat generated by the nuclear fusion reaction is also absorbed by the blanket and is transferred to the coolant, the thermal properties of breeder materials, such as enthalpy and heat capacity, are of primary importance for the design of a blanket system [1].

Lithium metatitanate of the composition Li_2TiO_3 ($M = 109.76$) is taken into account as breeding material. It has a homogeneity range and exists in three solid modifications, α, β and γ [2,3]. The α phase is metastable and has a monotropic transformation at about 300°C. The low-temperature β-Li_2TiO_3 phase is monoclinic, has a homogeneity range between 47 and 51 mol% TiO_2 [2] and 52 mol% [3], respectively, and crystallises in the Li_2SnO_3 type structure with the space group C2/c (No. 15), $Z = 8$, and the lattice parameters $a = 504.1$ pm, $b = 880.6$ pm, $c = 972.7$ pm, $\beta = 100.0°$ [4]. The room temperature X-ray density is $\rho_X = 3.43$ Mg/m^3 [4]. The high-temperature γ-Li_2TiO_3 phase is cubic and crystallises in the NaCl type structure, $Z = 4/3$, with the room temperature lattice parameter $a = 415.05$ pm. The X-ray density is $\rho_X = 3.40$ Mg/m^3. The enantiotropic β–γ transformation is reported at 1215°C [2], 1150°C [3] and 1212°C [5], respectively. The γ phase has a broad homogeneity range between 43 and 64 mol% TiO_2 at these temperatures.

The enthalpy of Li_2TiO_3 was measured by drop calorimetry between 388 and 1856 K [5]. The heat capacity of stoichiometric β-Li_2TiO_3 was determined by the laser flash method up to 1000 K [6], by differential scanning calorimetry (DSC) up to 1100 K [7] and by DSC up to 1000 K on non-stoichiometric material with Li/Ti = 1.9 [8,9]. The two properties were mutually converted by the author of this paper, they are compiled in Tables 1 and 2, respectively. The enthalpy of the β–γ transformation was evaluated from the enthalpy measurements of the modifications by drop calorimetry resulting in $\Delta_{tr}H = 11.5$ kJ/mol [5]. The tables contain further the enthalpy, the heat capacity and the enthalpy of β–γ transformation data of Li_2TiO_3 assessed by Barin [10] which are based on the work of Christensen et al. [5].

* Corresponding author. Tel.: +49-7247 82 2888; fax: +49-7247 82 4567.

E-mail address: heiko.kleykamp@imf.fzk.de (H. Kleykamp).

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Table 1
Enthalpy $H°(T) - H°(298\ K)$ of monoclinic and cubic Li_2TiO_3

T (K)	$H°(T) - H°(298\ K)$ (J/mol)				
	Barin [10]	Christensen et al. [5]	Davis and Haasz [6]	Saito et al. [7]	Kleykamp [11,12]
298	0	0	0	0	0
300	204	–	218	212	218
400	12 207	12 134	11 610	11 239	11 973
500	25 398	25 271	23 974	23 045	24 834
600	39 277	39 204	37 310	35 594	38 358
700	53 644	53 597	51 618	48 849	52 357
800	68 387	68 325	66 898	62 774	66 736
900	83 432	83 345	83 150	77 331	81 442
1000	98 722	98 617	100 374	92 484	96 443
1100	114 212	114 098	–	108 197	111 721
1200	129 866	129 788	–	–	127 260
1300	145 655	145 603	–	–	143 052
1400	161 556	161 502	–	–	159 090
1410	–	–	–	–	160 706(β)
1410	–	–	–	–	169 653(γ)
1485	175 149(β)	175 100(β)	–	–	–
1485	186 655(γ)	186 606(γ)	–	–	–
1500	189 300	189 242	–	–	183 355
1600	207 124	207 066	–	–	199 067
1700	225 282	225 225	–	–	215 313
1800	243 775	243 718	–	–	–
Method	Crit. tables	Drop calorimetry	Laser flash	DSC	Drop calorimetry

Table 2
Heat capacity C_p of monoclinic and cubic Li_2TiO_3

T (K)	C_p (J/K mol)					
	Barin [10]	Christensen et al. [5]	Davis and Haasz [6]	Roux [9]	Saito et al. [7]	Kleykamp [11,12]
298	109.9	111.0	108.9	113	106.1	108.6
300	110.4	111.5	109.1	114	106.3	109.1
400	127.3	127.4	118.8	131	114.2	124.2
500	135.8	135.7	128.5	139	126.4	132.4
600	141.5	141.0	138.2	146	129.1	137.8
700	145.7	144.8	147.9	152	136.0	142.0
800	149.0	148.0	157.7	159	142.5	145.5
900	151.8	150.7	167.4	167	148.6	148.6
1000	154.0	153.1	177.1	173	154.4	151.4
1100	155.8	155.3	–	–	159.8	154.1
1200	157.3	157.4	–	–	–	156.7
1300	158.5	159.4	–	–	–	159.2
1400	159.5	161.4	–	–	–	161.6
1410	–	–	–	–	–	161.8(β)
1410	–	–	–	–	–	150.0(γ)
1485	160.3(β)	163.0(β)	–	–	–	–
1485	176.1(γ)	176.1(γ)	–	–	–	–
1500	176.6	176.6	–	–	–	154.5
1600	179.9	179.9	–	–	–	159.8
1700	183.3	183.3	–	–	–	165.2
1800	186.6	186.6	–	–	–	–
Method	Crit. tables	Drop calorimetry	Laser flash	DSC	DSC	Drop calorimetry

2. Experimental

2.1. Materials

Lithium oxide granules (99.5% purity) and titanium dioxide powder (99.9% purity), both from Alfa Aesar, Karlsruhe, were mixed in equimolar composition and compacted in an argon-filled glove box and repeatedly arc-melted under reduced argon pressure by turning over the buttons. They were then annealed at 900°C for 24 h under argon and thereafter at 950°C for 1 h under dry air to remove absorbed H_2O and CO_2. The X-ray diffraction analysis by the Guinier method was applied using Cu $K\alpha_1$ radiation ($\lambda = 154.060$ pm) and an internal NaCl standard (lattice parameter $a = 564.02$ pm) for calibration. The product is single-phase, monoclinic $Li_2 TiO_3$ with the lattice parameters $a = (505.4 \pm 0.5)$ pm, $b = (877.9 \pm 0.7)$ pm, $c = (975.7 \pm 1.1)$ pm and $\beta = (100.1 \pm 0.1)°$. The chemical analysis results in 48.2 mol% Li_2O, 51.3 mol% TiO_2 and 0.5 mol% other oxides which corresponds to the normalised formula $Li_{1.92}$ $Ti_{1.02}O_3$. The composition is shifted to the TiO_2 rich phase boundary due to the predominant Li_2O evaporation during arc-melting.

2.2. Calorimetry

The enthalpy measurements on Li_2TiO_3 specimens (51.3 mol% TiO_2) in the 80–120 mg range were carried out in the isothermal mode of the high-temperature calorimeter HTC 1800 (Setaram S.A., Lyon, France) between 124°C and 1377°C by dropping the specimens from the introducer at 25°C into the preheated working crucible. The calibration of the calorimeter was determined using the tabulated enthalpy of α-Al_2O_3 [10]. In these experiments platinum liners were used inside the Al_2O_3 working and reference crucibles in order to reduce the S.D. of calibration and measurement. This action achieved a more uniform heat flux through the crucible walls. The enthalpy of transformation of Li_2TiO_3 (51.3 mol% TiO_2) was obtained on about 500 mg specimens in the anisothermal mode of the calorimeter with a heating rate of 2 K/min between 1100°C and 1230°C. The calibration was realised using the tabulated enthalpies of melting of gold and nickel. A platinum liner was not used in this experiment to avoid reactions with the standard specimens. Details of the sensitivity factor determination are described in [11]. The calibration as a function of temperature is graphically presented in [12].

3. Results

3.1. Enthalpy

The enthalpy $H°(T) - H°(298\ \mathrm{K})$ of β- and γ-Li_2TiO_3 was measured in the isothermal mode between 397 and 1650 K. Mass losses of 0.3% were observed after the experiment at the maximum temperature 1650 K. Two smoothed enthalpy curves of the experimental results presented in Table 3 were fitted to polynomials, $H°(T) - H°(298\ \mathrm{K}) = a + bT + cT^2 + dT^{-1}$ by the least squares method which give $H°(T) - H°(298\ \mathrm{K}) = -49\,181 + 131.876T + 0.011097T^2 + 2\,651\,112T^{-1}$ J/mol (298–1410 K) for monoclinic β-Li_2TiO_3 and $H°(T) - H°(298\ \mathrm{K}) = +49\,729 + 50.517T + 0.031679T^2 - 20\,143\,786T^{-1}$ J/mol (1410–1700 K) for cubic γ-Li_2TiO_3. The interpolated β–γ transformation temperature of Li_2TiO_3 (51.3 mol% TiO_2) is 1410 K (1137°C). The 68% S.D. of the experimental data is 1.6%. The enthalpy is given in 100 K intervals in Table 1.

Table 3
Experimental results of the enthalpy of monoclinic and cubic Li_2TiO_3

T (K)	$H°(T) - H°(298\ \mathrm{K})$ (J/mol)		Dev. (%)
	Experimental	Calculated	
397	11 499	11 601	−0.88
452	18 856	18 560	1.57
502	24 766	25 099	−1.34
551	32 624	31 663	2.94
604	38 822	38 910	−0.23
650	45 359	45 306	0.12
704	52 005	52 926	−1.77
755	60 622	60 223	0.66
802	64 290	67 027	−4.26
845	73 784	73 316	0.63
900	80 869	81 442	−0.71
948	89 056	88 607	0.50
1001	98 936	96 595	2.37
1047	102 739	103 590	−0.83
1092	109 848	110 489	−0.58
1121	118 073	114 962	2.63
1159	121 721	120 858	0.71
1199	128 084	127 103	0.77
1247	135 118	134 651	0.35
1287	142 492	140 985	1.06
1332	149 905	148 157	1.17
1348	147 473	150 720	−2.20
1372	155 211	154 575	0.41
1387	154 174	156 991	−1.83
1396	157 462	158 444	−0.62
1414	170 541	170 255	0.17
1424	169 389	171 759	−1.40
1453	177 069	176 149	0.52
1473	182 499	179 202	1.81
1497	182 797	182 892	−0.05
1523	187 314	186 922	0.21
1554	189 841	191 774	−1.02
1575	194 743	195 089	−0.18
1601	199 075	199 227	−0.08
1624	200 059	202 916	−1.43
1650	210 405	207 122	1.56

3.2. Heat capacity

The heat capacity $C_p(T)$ of β- and γ-Li_2TiO_3 was evaluated by differentiation of the enthalpy polynomials which results in $C_p = 131.876 + 0.022194T - 2651\,112T^{-2}$ J/K mol (298–1410 K) for monoclinic β-Li_2TiO_3 and $C_p = 50.517 + 0.063358T + 20\,143\,786T^{-2}$ J/K mol (1410–1700 K) for cubic γ-Li_2TiO_3. The heat capacity is given in 100 K intervals in Table 2. The value at 298 K is C_p (298 K) = (108.6 ± 2.5) J/K mol. It should be noted that the result at 298 K is an extrapolated value from the experimental temperature range above 397 K, further, that the heat capacity of the cubic modification is lower than that of the monoclinic modification at the transition temperature. The specific heat capacity c_p results are plotted as a function of temperature in Fig. 1.

3.3. Enthalpy of transformation

The enthalpy of the β–γ transformation of Li_2TiO_3 (51.3 mol% TiO_2) results from the difference of the enthalpies of Li_2TiO_3 at the interpolated transformation temperature $T_{tr} = 1137$°C which gives $\Delta_{tr}H = (8950 \pm 180)$ J/mol. The result of the direct enthalpy of transformation measurement by anisothermal calorimetry is presented in Fig. 2. The heat flow starts at 1137°C and is terminated at 1188°C yielding an integrated heat flow $Q = 21\,900$ μV s. The sensitivity factor at an intermediate temperature of 1160°C is $S = 0.49$ μV/mW. The

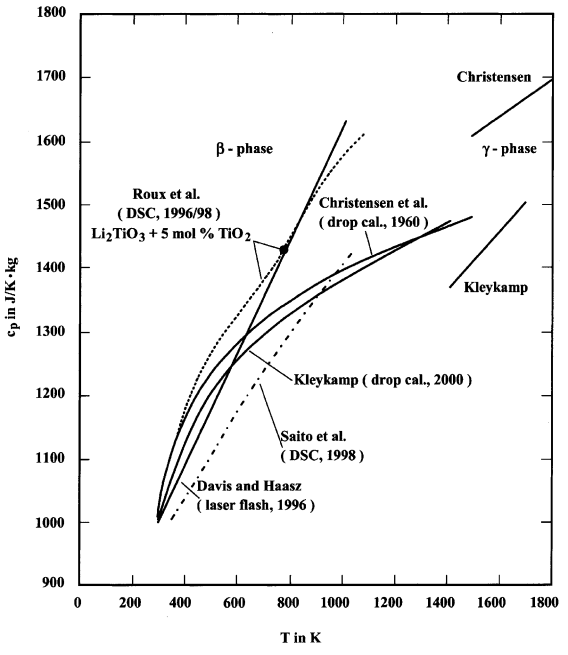

Fig. 1. Specific heat capacity c_p of Li_2TiO_3.

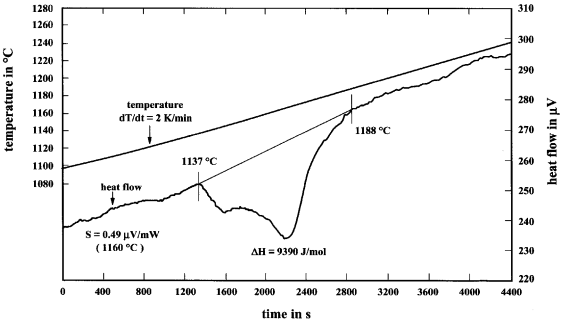

Fig. 2. Enthalpy of monoclinic–cubic transformation of Li_2TiO_3 by anisothermal calorimetry.

enthalpy of the β–γ transformation was evaluated from these Q/S data to $\Delta_{tr}H = (9390 \pm 350)$ J/mol. The heat flow curve in Fig. 2 can be split into two curves, the first one starting at 1137°C, the second one at about 1150°C. The β-Li_2TiO_3 phase has a homogeneity range and a congruent transformation temperature. The extrapolated value to stoichiometric Li_2TiO_3 is $T_{tr} = (1155 \pm 5)$°C. The high-temperature γ phase forms a eutectoid with $Li_4Ti_5O_{12}$ at 955°C. Hence, the used composition of β-Li_2TiO_3 (51.3 mol% TiO_2) deviating from the stoichiometric composition passes the phase boundary during heating, enters the β–γ two-phase field and ends in the single-phase γ-Li_2TiO_3 region. The observation of two peaks in Fig. 2 is explained by crossing two-phase boundaries due to the deviation from the stoichiometric composition of Li_2TiO_3.

4. Discussion

The enthalpy and the heat capacity of β-Li_2TiO_3 (73.77 mass% TiO_2) of this work agree well within the range of 2% difference with the results of Christensen et al. [5] (72.70 mass% TiO_2) who used also the drop calorimetry method. Slight deviations occur in the heat capacity of the cubic γ-Li_2TiO_3 above 1500 K where the data of this work are 10–12% lower than those of Christensen et al. An explanation of this discrepancy is difficult. Possibly, the statistical error of the enthalpy measurements in the γ phase is larger in Christensen's work with six experimental points compared with eleven points in this work. It is common physical experience that the heat capacity just above a solid–solid transformation temperature is lower due to the higher crystallographic symmetry (e.g. monoclinic–cubic transformation) and the higher vibrational frequency of phases with a cubic lattice. The heat capacity results determined directly by the laser flash method [6] as well as by the differential scanning method [7,8] up to about 1000 K diverge up to 17% from the drop calorimetry results.

The heat capacity of Li_2TiO_3 (73.77 mass% TiO_2) at 298 K is $C_p = (108.6 \pm 2.5)$ J/K mol. The Neumann–Kopp rule of the additive behaviour of the heat capacities of the binary constituent oxides is not fulfilled. The experimental results of the heat capacity of Li_2TiO_3 are up to 7% lower than the sum of the heat capacities of Li_2O and TiO_2. The deviation increases with temperature [10]. A similar behaviour was previously observed for the heat capacity of Li_2ZrO_3 [13].

The average of the enthalpy of the β–γ transformation measured by isothermal and anisothermal calorimetry is $\Delta_{tr}H = (9200 \pm 300)$ J/mol at about 1410 K. The transformation temperature of stoichiometric Li_2TiO_3 is extrapolated to $T_{tr} = (1428 \pm 5)$ K. This temperature is lower than that of Christensen et al. [5] $T_{tr} = 1485$ K, at which the β–γ phase change was complete upon heating.

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