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Enthalpies and heat capacities of Li_2SiO_3 and Li_2ZrO_3 between 298 and 1400 K by drop calorimetry [1]

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Abstract

The enthalpies of Li_2SiO_3 and Li_2ZrO_3 were measured between 368 and 1414 K by an isoperibol Setaram HTC 1800 drop calorimeter. The calibration procedure is described. The smoothed enthalpies between 298 and 1400 K are:

$$H^\circ_T - H^\circ_{298}\langle Li_2SiO_3\rangle = -51157 + 125.860T + 0.01713T^2 + 3614467T^{-1}\ \mathrm{J/mol}$$

$$H^\circ_T - H^\circ_{298}\langle Li_2ZrO_3\rangle = -46453 + 134.857T + 0.00740T^2 + 1671251T^{-1}\ \mathrm{J/mol}$$

The standard deviation is $\approx 3\%$. The heat capacities were derived by differentiation. The values extrapolated to 298 K are:

$$C_{p,298}\langle Li_2SiO_3\rangle = (95.4 \pm 3.1)\ \mathrm{J/K\ mol}$$

$$C_{p,298}\langle Li_2ZrO_3\rangle = (120.4 \pm 3.0)\ \mathrm{J/K\ mol}$$

INTRODUCTION

Lithium ceramics are being considered as possible solid breeder materials in the blanket of future fusion reactors. The role of the breeder materials is to produce tritium atoms, which act as fuel components of the reactor. As the heat generated by the nuclear fusion reaction is 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.

EXPERIMENTAL

Materials

The lithium metasilicate (Li_2SiO_3) as delivered had been prepared from an aqueous suspension of amorphous silicon dioxide and lithium hydroxide

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TABLE 1

X-ray diffraction patterns of Li_2SiO_3 at room temperature

hkl	d_{obs}/pm	Rel. intensity	d_{calc}/pm
020	468	v. st.	469.80
110			468.53
111	330.3	v. st.	330.45
130	270.9	v. st.	270.99
200			270.26
131	234.2	st.	234.28
220			234.26
002	233.00	st.	233.07
022	208.79	m.	208.79
112			208.67
150	177.44	w.	177.50
310	176.95	m.	176.95
132			176.70
202	176.41	m.	176.50
241	165.69	m.	165.71
311			176.43
060	156.65	m.	156.60
330	156.02	m.	156.18
113	147.45	w.	147.48
152	141.26	w.	141.21
242			141.11
312	140.98	w.	140.93
260	135.52	w.	135.50
133	134.94	m.	134.79
350	130.05	m.	130.05
062			129.98
223	129.52	m.	129.49
171	125.44	w.	125.46

which gave X-ray amorphous $Li_2SiO_3 \cdot H_2O$. This was followed by spray drying and by calcination above 250°C [1]. The product comprised a single phase. Li_2SiO_3 is orthorhombic, space group $Cmc2_1$ (No. 36) [2–4]. The material was granulated, re-compacted and annealed at 900°C for 2 h in air to remove absorbed H_2O and CO_2 immediately before the X-ray diffraction and enthalpy measurements. X-ray diffraction was carried out at room temperature by the Guinier method with Cu $K\alpha_1$ radiation ($\lambda = 154.060$ pm) and calibration with an internal NaCl standard ($a = 564.02$ pm). The positions of the diffraction lines were determined with a Huber comparator, the intensities being estimated by visual examination. The lattice parameters were calculated by an optimization programme which gave the results $a = (540.5 \pm 0.1)$ pm, $b = (939.6 \pm 0.2)$ pm, $c = (466.1 \pm 0.1)$ pm. The X-ray diffraction pattern is given in Table 1.

TABLE 2

X-ray diffraction patterns of Li_2ZrO_3 at room temperature

hkl	d_{obs}/pm	Rel. intensity	d_{calc}/pm
020	451.4	m.	451.53
110	437.3	v. st.	437.83
−111	404.98	st.	403.83
021	335.71	v. st.	335.28
111	285.37	m.	285.33
130	257.88	st.	257.97
−112			257.95
−131	250.42	st.	250.46
200			250.30
002			250.28
−221	231.33	st.	231.12
040	225.76	v. st.	225.76
−202			225.74
220	218.88	m.	218.92
022			218.90
131	212.72	v. st.	212.75
041	205.63	m.	205.80
−222	201.71	w.	201.92
112	191.22	m.	191.28
221	179.62	m.	179.58
−311	177.05	m.	177.04
−113			177.03
−241	173.15	w.	172.98
150	169.88	st.	169.89
−312			169.88
−151	167.75	st.	167.69
240			167.65
042			167.64
310	164.08	m.	164.09
132			164.09
−223	161.49	st.	161.52
−242	159.64	m.	159.63
023	156.50	m.	156.51
151	154.90	st.	154.83
−331			154.83
−133			154.82

The delivered lithium metazirconate (Li_2ZrO_3) had been prepared by reaction of lithium hydroxide and zirconium *n*-propoxide in methanol. The product was obtained by substitution of the alcohol by water and by spray drying. This was followed by calcination at 650°C for 2 h in air [5]. The product consisted of a single phase. Li_2ZrO_3 is very hygroscopic and exists between 750 and 1000°C under normal pressure only in one modification [6]; it is monoclinic, space group *Cc* (No. 9) [7] or *C*2/*c* (No. 15) [8]. The

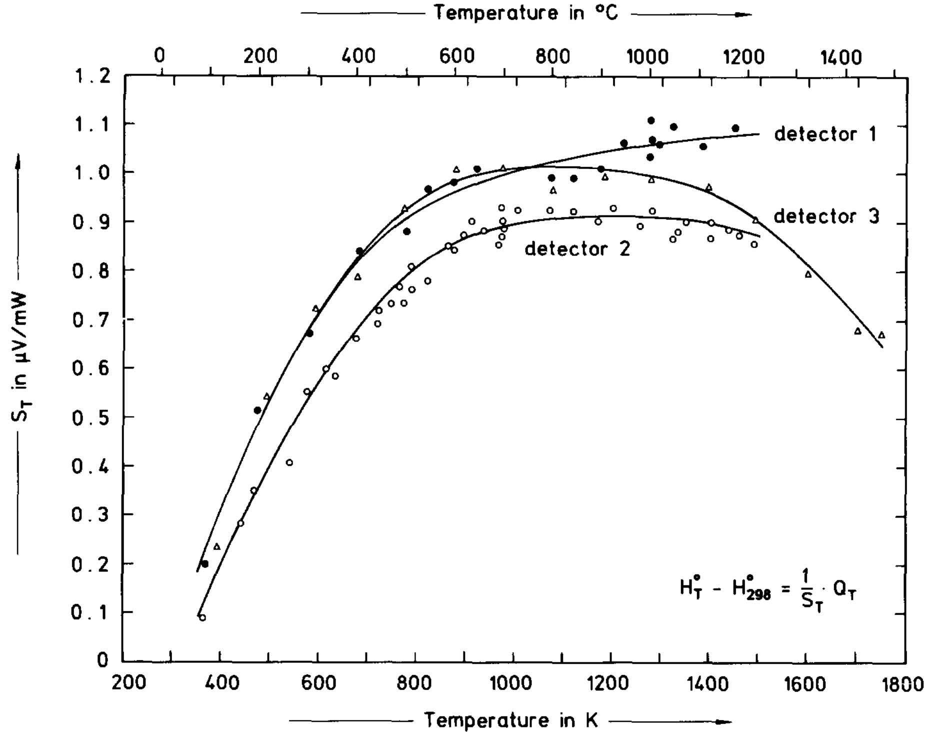

Fig. 1. Sensitivity factor S_T as a function of temperature of the Setaram HTC 1800 calorimeter measured with α-Al_2O_3 in different detectors.

material was granulated, re-compacted and annealed at 900°C for 2 h in air to remove H_2O and CO_2 before the X-ray diffraction and enthalpy measurements. The obtained lattice parameters were $a = (542.5 \pm 0.1)$ pm, $b = (903.1 \pm 0.2)$ pm, $c = (542.5 \pm 0.1)$ pm, $\beta = (112.65 \pm 0.02)°$. The X-ray diffraction pattern is given in Table 2.

Calorimetry

The enthalpy measurements were carried out by the drop method using the high temperature calorimeter HTC 1800 from the manufacturer Setaram S.A. (Lyon, France). The calorimeter is an instrument of the isoperibol type and operates according to the heat flow principle [9]. The detector is made up of two alumina crucibles, one above the other, which are surrounded by two crown-shaped piles of 18 + 18 Pt-6% Rh/Pt-30% Rh thermocouples, each pile in one axial plane. Isothermal measurements were made under argon by dropping samples of mass around 100 mg and initially at room temperature (25°C) through a lock into the working cell of the preheated calorimeter. The temperature drift was < 0.5 K in 1 h.

TABLE 3

Experimental results of the enthalpy of Li_2SiO_3

T/K	$H^\circ_T - H^\circ_{298}$/(J/mol)		Deviation/%
	Exp.	Calc.	
372	7613	7750	−1.80
445	16751	16366	2.30
475	19968	20102	−0.67
551	31625	29953	5.29
578	33359	33567	−0.62
638	41668	41781	−0.27
679	45686	47524	−4.02
747	56932	57259	−0.57
823	68307	68422	−0.17
923	84062	83523	0.64
970	89301	90773	−1.65
1072	109769	106825	2.68
1123	114125	115008	−0.77
1175	125851	123458	1.90
1222	132614	131185	1.08
1277	135254	140334	−3.76
1313	146802	146385	0.28
1342	146534	151295	−3.25
1379	167971	157609	6.17
1411	152531	163102	−6.93
1414	174723	163619	6.36

The quality of the instrument is characterized by the sensitivity factor S_T, which is the proportionality factor between the measured heat Q_T consumed by the sample from the surroundings, given in millivolt seconds per mole of the sample, and by the molar enthalpy $H^\circ_T - H^\circ_{298}$ given in J/mol:

$$Q_T = S_T(H^\circ_T - H^\circ_{298})$$

The calibration was effected by use of the tabulated enthalpy of α-Al_2O_3 [10]. Spheres (sapphire, NIST quality), were used with a mass of about 60 mg. The sensitivity factor given in μV/mW was determined up to 1750 K. It is strongly temperature dependent and increases for the preselected electronic amplification up to 1.0 μV/mW at 800 K, passes through a flat maximum and then falls to $\approx$ 0.7 μV/mW at 1750 K owing to increased heat loss by radiation; see Fig. 1. The sensitivity factor is further dependent on the type of detector and on the axial position (height) of the sample in the crucible within a series of successive drops. The background signal is below 0.5 μV. With a sensitivity factor $S = 1$ μV/mW, this gives a detection limit close to 0.5 mW.

TABLE 4

Experimental results of the enthalpy of Li_2ZrO_3.

T/K	$H^\circ_T - H^\circ_{298}$/(J/mol)		Deviation/%
	Exp.	Calc.	
368	8541	8718	−2.07
448	20052	19179	4.36
545	32974	32309	2.02
615	40456	42000	−3.82
674	49534	50282	−1.51
768	64582	63658	1.43
802	70227	68545	2.39
829	71966	72445	−0.66
866	74763	77812	−4.08
900	81322	82769	−1.78
909	85837	84084	2.04
967	92722	92601	0.13
999	95491	97326	−1.92
1003	96243	97918	−1.74
1025	99985	101180	−1.19
1052	109000	105194	3.49
1071	110096	108026	1.88
1107	118014	113411	3.90
1115	113929	114610	−0.60
1168	119342	122585	−2.72
1207	136340	128483	5.76
1254	135987	135625	0.27
1306	141346	143570	−1.57
1309	143485	144030	−0.38
1380	152180	154951	−1.82
1410	159308	159591	−0.18

The enthalpies of each Li_2SiO_3 and Li_2ZrO_3 sample were measured at a preselected temperature by a preceding and a subsequent calibration of the instrument with α-Al_2O_3. The average of the two calibrations was taken for calculation of the sensitivity factor of the corresponding enthalpy measurement.

RESULTS

The enthalpies $H^\circ_T - H^\circ_{298}$ of Li_2SiO_3 and Li_2ZrO_3 were measured in the temperature ranges 372–1414 K and 368–1410 K respectively. Mass losses up to 0.5% after the experiments were observed above these temperatures. The experimental results compiled in Tables 3 and 4 were fitted to a polynomial by the least squares method using $H^\circ_T - H^\circ_{298} = a + b \cdot T + c \cdot T^2 + d \cdot T^{-1}$, which gives

TABLE 5

Enthalpy $H^\circ_T - H^\circ_{298}$ of Li_2SiO_3

T/K	$H^\circ_T - H^\circ_{298}/(J/mol)$			
	Barin [13]	Bennington et al. [11]	Brandt and Schulz [12]	Kleykamp (this work)
298	0	0	0	0
300	186	184	195	191
400	11312	11284	11258	10965
500	23677	23845	23913	23285
600	36796	37371	37490	36551
700	50501	51610	51703	50503
800	64710	66379	66407	65014
900	79363	81630	81523	80010
1000	94411	97278	97003	95450
1100	109808	113240	–	111305
1200	125518	129537	–	127557
1300	141513	(146105)	–	144194
1400	157775	(162904)	–	161207
Method	crit. tables	drop cal.	DSC	drop cal.

TABLE 6

Enthalpy $H^\circ_T - H^\circ_{298}$ of Li_2ZrO_3

T/K	$H^\circ_T - H^\circ_{298}/(J/mol)$			
	Barin [13]	Hollenberg and Baker [15]	Cordfunke et al. [15]	Kleykamp (this work)
298	0	0	0	0
300	203	258	216	241
400	12254	13396	12422	12852
500	25661	27010	25600	26168
600	39874	41102	39411	39911
700	54657	55671	53712	53960
800	69890	70717	68428	68257
900	85509	–	(83527)	82769
1000	101473	–	(98967)	97474
1100	117758	–	–	112362
1200	134347	–	–	127423
1300	151229	–	–	142651
1400	168394	–	–	158043
1500	185838	–	–	–
Method	crit. tables	DSC	adiab. + drop cal.	drop cal.

TABLE 7

Heat capacity C_p of Li_2SiO_3

T/K	C_p/(J/K mol)			
	Barin [13]	Bennington et al. [11]	Brandt and Schulz [12]	Kleykamp (this work)
298	100.5	99.9	97.5	95.4
300	101.0	100.4	98.2	96.0
400	118.8	119.5	120.3	117.0
500	127.8	131.0	131.8	128.5
600	134.3	139.1	139.3	136.4
700	139.7	145.3	144.8	142.5
800	144.4	150.3	149.2	147.6
900	148.6	154.5	153.0	152.2
1000	152.3	158.2	156.5	156.5
1100	155.6	161.4	–	160.6
1200	158.6	164.3	–	164.5
1300	161.3	(166.9)	–	168.3
1400	163.9	(169.1)	–	172.0
Method	crit. tables	drop cal.	DSC	drop cal.

$$H^\circ_T - H^\circ_{298}\langle Li_2SiO_3\rangle = -51157 + 125.860T + 0.01713T^2 + 3614467T^{-1}\ \text{J/mol}$$

$$H^\circ_T - H^\circ_{298}\langle Li_2ZrO_3\rangle = -46453 + 134.857T + 0.00740T^2 + 1671251T^{-1}\ \text{J/mol}$$

between 298 and 1400 K. The 68% standard deviations of the experiments are 3.3% and 2.5% respectively. The enthalpies of Li_2SiO_3 and Li_2ZrO_3 are given numerically in 100 K intervals in Tables 5 and 6.

The heat capacities of Li_2SiO_3 and Li_2ZrO_3 were evaluated by differentiation of the enthalpy polynomials, which gives

$$C_{p,T}\langle Li_2SiO_3\rangle = 125.860 + 0.03426T - 3614467T^{-2}\ \text{J/K mol}$$

$$C_{p,T}\langle Li_2ZrO_3\rangle = 134.857 + 0.01480T - 1671251T^{-2}\ \text{J/K mol}$$

The heat capacities of Li_2SiO_3 and Li_2ZrO_3 are illustrated as a function of temperature in Figs. 2 and 3 and are given numerically in 100 K intervals in Tables 7 and 8. The heat capacities at 298 K are

$$C_{p,298}\ \langle Li_2SiO_3\rangle = (95.4 \pm 3.1)\ \text{J/K mol}$$

$$C_{p,298}\langle Li_dZrO_3\rangle = (120.4 \pm 3.0)\ \text{J/K mol}$$

It should be noted that the results at 298 K are extrapolated values from the experimental temperature range above 368 K.

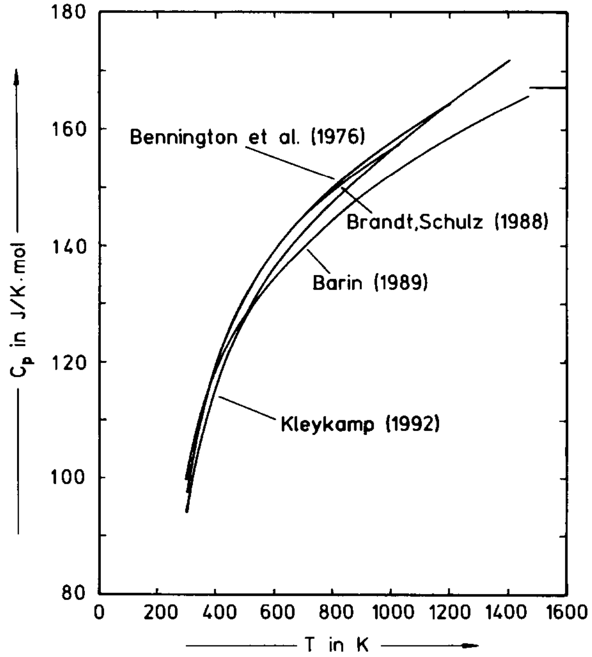

Fig. 2. Heat capacity C_p of Li_2SiO_3.

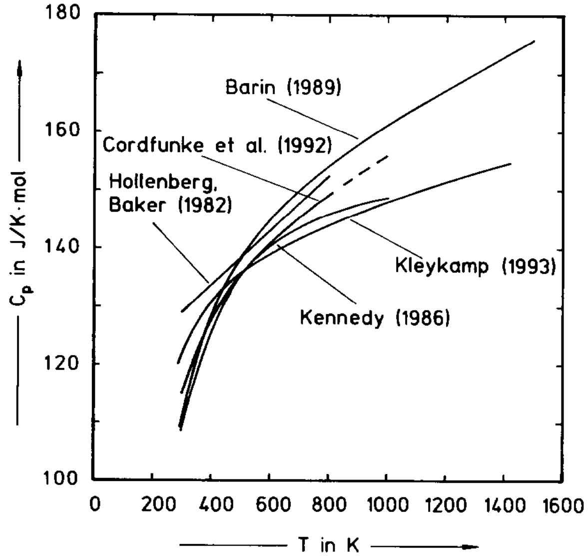

Fig. 3. Heat capacity C_p of Li_2ZrO_3.

TABLE 8

Heat capacity of C_p of Li_2ZrO_3

T/K	C_p/(J/K mol)				
	Barin [13]	Hollenberg and Baker [15]	Kennedy [16]	Cordfunke et al. [14]	Kleykamp (this work)
298	109.5	128.9	110	114.6	120.4
300	110.0	129.0	110	114.9	120.7
400	128.7	133.8	126	127.8	130.3
500	138.7	138.5	135	135.3	135.6
600	145.2	143.3	141	140.7	139.1
700	150.2	148.1	144	145.2	141.8
800	154.3	(152.8)	146	149.1	144.1
900	158.0	–	147	(152.7)	146.1
1000	161.3	–	(149)	(156.2)	148.0
1100	164.4	–	–	–	149.8
1200	167.4	–	–	–	151.5
1300	170.2	–	–	–	153.1
1400	173.1	–	–	–	154.7
1500	175.8	–	–	–	–
Method	crit. tables	DSC	DSC	adiab. + drop cal.	drop cal.

DISCUSSION

The enthalpy of Li_2SiO_3 has so far been measured by Bennington et al. [11] by drop calorimetry in the temperature range 298–1404 K. The heat capacity was calculated by differentiation of the enthalpy. The heat capacity of Li_2SiO_3 was determined by Brandt and Schulz [12] by differential scanning calorimetry in the range 298–1000 K. The enthalpy was evaluated by integration of the heat capacity. The thermodynamic data of these authors [11,12] compiled in Tables 5 and 7 agree well with the enthalpy and the heat capacity measured in this study. However, the experimental results at temperatures above 500 K are higher than the enthalpy and the heat capacity of Li_2SiO_3 estimated by Barin [13] and in the JANAF tables [10], which were generated by application of Neumann–Kopp's rule to the constituent oxides Li_2O and SiO_2; see Fig. 2.

The enthalpy of Li_2ZrO_3 was measured previously by Cordfunke et al. [14] by drop calorimetry in the range 477–815 K. The heat capacity was calculated by differentiation of the enthalpy and the data were extrapolated to 1000 K. Low temperature heat capacity measurements between 6 and 372 K were made by adiabatic calorimetry [14]. The heat capacity of Li_2ZrO_3 was determined by Hollenberg and Baker [15] by differential scanning calorimetry between 350 and 750 K. The enthalpy in Table 6 was calculated by use of Hollenberg and Baker's analytical expression for the heat capacity, $c_p = 0.179 + 7.45 \times 10^{-5}T + 1.126T^{-2}$ cal/K g. Other heat capacity data on Li_2ZrO_3 obtained by differential scanning calorimetry were reported by Kennedy [16] in graphical form between 300 and 900 K. The enthalpy could not be obtained by integration of these measurements. The thermodynamic data of these authors [14–16] compiled in Tables 6 and 8 are somewhat higher than the enthalpy and the heat capacity measured in this study. However, all experimental results at temperatures above 500 K are lower than the enthalpy and the heat capacity of Li_2ZrO_3 given by Barin [13], which are based on an estimate by Kubaschewski [17]. The heat capacity of Li_2ZrO_3 is illustrated in Fig. 3.

The experiments on the enthalpy of Li_2SiO_3 and Li_2ZrO_3 between 298 and 1400 K have demonstrated that the use of a Setaram HTC 1800 calorimeter (1987/89 series) in this laboratory gives results with a temperature average 68% standard deviation of not less than 2.5%. This can be attributed to the short isothermal zone in the z-direction of the furnace and to the arrangement of the thermopile for the crucible of the detector in one plane perpendicular to the z-axis. It is hoped that these deficiencies will be eliminated in the present version of the instrument.

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