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Letter to the Editors

Enthalpy and heat capacity of $LiAlO_2$ between 298 and 1700 K by drop calorimetry

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Abstract

The enthalpy of γ-$LiAlO_2$ was measured between 403 and 1673 K by isothermal drop calorimetry. The smoothed enthalpy curve between 298 and 1700 K results in $H^0(T) - H^0(298\ \mathrm{K}) = -37\,396 + 93.143 \cdot T + 0.00557 \cdot T^2 + 2\,725\,221 \cdot T^{-1}$ J/mol. The standard deviation is 2.2%. The heat capacity was derived by differentiation of the enthalpy curve. The value extrapolated to 298 K is $C_{p,298} = (65.8 \pm 2.0)$ J/K mol.

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].

Also lithium aluminate of the composition $LiAlO_2$ ($M = 65.92$) is taken into account as breeding material. It is a line compound and exists in three modifications, α, β, and γ. The low-temperature α-modification [2–4] and the β-modification [5] transform at ambient pressure monotropically to the high-temperature γ-modification at elevated temperatures starting at about 250°C [6] or at about 700°C [7]. This phase crystallizes in a tetragonal structure, space group $P4_12_12$ (No. 92), $Z = 4$, with the room temperature lattice parameters $a = 516.87$ pm and $c = 629.79$ pm [8], and in the space group $P42_12$ (No. 90), $Z = 4$, with $a = 517.15$ pm and $c = 628.40$ pm [9], respectively.

The enthalpy of γ-$LiAlO_2$ was measured by drop calorimetry between 400 and 1800 K [10] and between 300 and 1000 K [11]. The specific heat capacity of γ-$LiAlO_2$ was determined by differential scanning calorimetry between 350 and 750 K [12] and between 300 and 1000 K [13]. The two properties were mutually converted by the author of this paper, they are compiled in Tables 1 and 2, respectively. The tables contain further the enthalpy and heat capacity data assessed by Barin [14], which are only based on the work of Christensen et al. [10].

2. Experimental

2.1. Materials

Lithium aluminate powder was supplied from Alfa Johnson Matthey GmbH, Karlsruhe. The chemical analysis yields: 10.29 mass% Li, 40.64 mass% Al, 0.71 mass% loss on ignition (900°C, 30 min), oxygen: balance. The data (normalised to 100%) results in 24.7 at.% Li, 25.1 at.% Al and 50.2 at.% O corresponding to the formula $LiAlO_2$. The material was compacted and annealed at 900°C for 10 min in dry air to relieve stresses, to attain complete recrystallization and to remove adsorbed H_2O and CO_2, immediately before X-ray diffraction and calorimetric measurements. X-ray diffraction was carried out at room temperature by the

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Table 1
Enthalpy $H^0(T) - H^0(298\ K)$ of γ-$LiAlO_2$

T in K	$H^0(T) - H^0(298\ K)$ in J/mol					
	Barin (1995)	Christensen et al. (1960)	Hollenberg, Baker (1982)	Brandt, Schulz (1988)	Asou et al. (1990)	Kleykamp (1999)
298	0	0	0	0	0	0
300	126	–	127	132	131	132
400	7701	7489	6961	7557	7743	7565
500	16 232	15 941	14 455	15 998	16 319	16 018
600	25 301	25 104	22 411	25 022	25 451	25 037
700	34 730	34 644	30 746	34 444	34 964	34 427
800	44 429	44 434	(39 415)	44 170	44 773	44 090
900	54 349	54 392	–	54 150	54 827	53 973
1000	64 460	64 517	–	64 352	65 097	64 044
1100	74 744	74 684	–	–	–	74 280
1200	85 187	85 270	–	–	–	84 670
1300	95 781	95 855	–	–	–	95 202
1400	106 519	106 608	–	–	–	105 871
1500	117 397	117 487	–	–	–	116 671
1600	128 412	128 491	–	–	–	127 599
1700	139 560	139 620	–	–	–	138 652
1800	150 841	150 875	–	–	–	–
Method	Crit. tables	Drop cal.	DSC	DSC	Drop cal.	Drop cal.

Guiner method with Cu Kα_1 radiation ($\lambda = 154.060$ pm) and calibration with an internal NaCl standard (lattice parameter $a = 564.02$ pm). The material is single-phase. The lattice parameters were calculated by an optimisation programme to be $a = (516.2 \pm 0.2)$ pm and $c = (626.3 \pm 0.3)$ pm which are slightly smaller than the previously published results [8,9]. Four formula units form the tetragonal elementary cell. The X-ray density was calculated to be $\rho_x = 2.62$ Mg/m^2.

2.2. Calorimetry

The enthalpy measurements of γ-$LiAlO_2$ specimens in the 50 mg range were carried out in the isothermal

Table 2
Heat capacity C_p of γ-$LiAlO_2$

T in K	C_p in J/K mol					
	Barin (1995)	Christensen et al. (1960)	Hollenberg, Baker (1982)	Brandt, Schulz (1988)	Asou et al. (1990)	Kleykamp (1999)
298	67.8	67.7	63.5	65.9	68.2	65.8
300	68.2	68.1	63.7	66.3	68.6	66.2
400	81.6	81.5	72.1	80.4	81.6	80.6
500	88.4	88.4	77.4	87.8	88.9	87.8
600	92.7	92.7	81.5	92.4	93.4	92.3
700	95.7	95.8	85.1	95.9	96.7	95.4
800	98.2	98.2	(88.3)	98.6	99.4	97.8
900	100.2	100.2	–	100.9	101.7	99.8
1000	102.0	102.0	–	103.1	103.7	101.6
1100	103.6	103.7	–	–	–	103.1
1200	105.2	105.2	–	–	–	104.6
1300	106.7	106.7	–	–	–	106.0
1400	108.1	108.1	–	–	–	107.4
1500	109.5	109.5	–	–	–	108.6
1600	110.8	110.8	–	–	–	109.9
1700	112.1	112.1	–	–	–	111.1
1800	113.5	113.4	–	–	–	–
Method	Crit. tables	Drop cal.	DSC	DSC	Drop cal.	Drop cal.

mode of the high-temperature calorimeter HTC 1800 (manufacturer: Setaram S.A., Lyon, France) between 130 and 1400°C by dropping the specimens from the introducer at 25°C into the preheated working crucible. The calibration of the calorimeter was determined with the known enthalpy of α-Al_2O_3 [14]. Details of the sensitivity factor determination are described in Ref. [15]. Platinum liners were used inside the Al_2O_3 working and reference crucibles in these experiments in order to reduce the standard deviation of calibration and measurement. This was achieved by a more uniform heat flux through the crucible walls.

3. Results

The enthalpy $H^0(T) - H^0(298\ \mathrm{K})$ of $LiAlO_2$ was measured in the isothermal mode between 403 and 1673 K. Mass losses up to 0.5% were observed after the experiment above the upper temperature limit. A

Table 3
Experimental results of the enthalpy of γ-$LiAlO_2$

T in K	$H^0(T) - H^0(298\ \mathrm{K})$ in J/mol		Deviation in %
	Experimental	Calculated	
403	7892	7807	1.07
419	9022	9113	−1.00
421	9973	9278	6.97
448	11 634	11 533	0.87
465	12 387	12 981	−4.79
476	13 931	13 927	0.02
479	13 709	14 187	−3.49
491	14 741	15 230	−3.32
501	15 936	16 106	−1.07
523	18 439	18 052	2.10
551	20 729	20 563	0.80
576	23 570	22 834	3.12
601	24 710	25 130	−1.70
620	27 247	26 890	1.31
654	30 359	30 069	0.95
677	32 429	32 241	0.58
701	34 326	34 522	−0.57
721	36 239	36 436	−0.54
752	37 860	39 422	−4.12
776	41 261	41 750	−1.18
804	44 340	44 482	−0.32
825	47 628	46 542	2.28
861	50 508	50 095	0.82
900	53 598	53 973	−0.70
919	55 686	55 873	−0.34
949	58 220	58 886	−1.14
970	62 631	61 004	2.60
999	64 816	63 942	1.35
1008	67 194	64 857	3.48
1051	69 821	69 244	0.83
1096	72 017	73 868	−2.57
1125	75 817	76 864	−1.38
1150	79 074	79 457	−0.48
1175	81 900	82 059	−0.19
1222	88 876	86 975	2.14
1276	94 625	92 662	2.08
1345	99 688	99 987	−0.30
1409	108 695	106 838	1.71
1443	108 314	110 499	−2.02
1501	116 264	116 780	−0.44
1569	124 142	124 198	−0.05
1673	133 782	135 656	−1.40

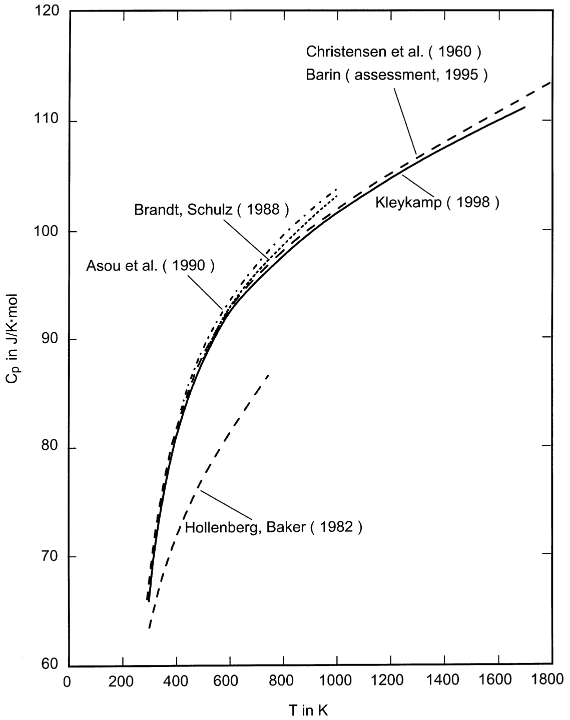

Fig. 1. Heat capacity C_p of γ-$LiAlO_2$ as a function of temperature.

smoothed enthalpy curve of the experimental points presented in Table 3 was fitted to polynomial $H^0(T) - H^0(298\ \mathrm{K}) = a + b \cdot T + c \cdot T^2 + d \cdot T^{-1}$ by the least squares method which gives $H^0(T) - H^0(298\ \mathrm{K}) = -37\,396 + 93.143 \cdot T + 0.00557 \cdot T^2 + 2\,725\,221 \cdot T^{-1}$ J/mol between 298 and 1700 K. The 68% standard deviation of the experimental data is 2.2%. The enthalpy is given in 100 K intervals in Table 1.

The heat capacity $C_p(T)$ of $LiAlO_2$ was evaluated by differentiation of the enthalpy polynomial which results in $C_p(T) = 93.143 + 0.01114 \cdot T - 2\,725\,221 \cdot T^{-2}$ J/K mol between 298 and 1700 K, see Fig. 1. The heat capacity is given in 100 K intervals in Table 2. The value at 298 K is $C_p(298\ \mathrm{K}) = (65.8 \pm 2.0)$ J/K mol. It should be noted that the result at 298 K is an extrapolated value from the experimental temperature range above 403 K.

4. Discussion

The enthalpy of γ-$LiAlO_2$ measured through drop calorimetry up to 1800 K by Christensen et al. [10] agrees very well with the date of this work. This result certifies the high quality of the commercial SETARAM calorimeters and the confidence of Christensen's pioneering work 40 years ago.

The enthalpy measured in this work is only less than 0.9% lower than the results of Christensen et al. [10] and Asou et al. [11] in the whole temperature range. The heat capacity of $LiAlO_2$ derived from the drop calorimetry measurements by differentiation of the enthalpy curve is less than 1.5% lower than the direct differential scanning calorimetry results of Brandt and Schulz [13] between room temperature and 1000 K. The agreement is excellent. The Neumann–Kopp rule of the additive behaviour of the heat capacities of the binary constituent oxides is fulfilled in the lower temperature region, however, the deviation from the experimental results of this work is from +4% to +5% between 1000 and 1700 K.

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