

The heat capacity and derived thermodynamic functions of La₂Zr₂O₇ and Ce₂Zr₂O₇ from 4 to 1000 K

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THE HEAT CAPACITY AND DERIVED THERMODYNAMIC FUNCTIONS OF $\text{La}_2\text{Zr}_2\text{O}_7$ AND $\text{Ce}_2\text{Zr}_2\text{O}_7$ FROM 4 TO 1000 K

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Abstract—The heat capacities of cerium and lanthanum zirconate ($\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Zr}_2\text{O}_7$) were measured from 4 to 400 K by adiabatic calorimetry. The derived thermodynamic functions, H° , S° and $\{G^\circ - H^\circ(0)\}/T$ were calculated. The standard molar entropies at 298.15 K were determined as $230.21 \pm 0.46 \text{ J/mol} \cdot \text{K}$ and $238.53 \pm 0.48 \text{ J/mol} \cdot \text{K}$.

Enthalpy increments relative to 298.15 K were measured by drop calorimetry from 500 to 900 K. From these data the thermodynamic functions, including the enthalpy and Gibbs free energy of formation of the two compounds were derived for temperatures up to 1000 K. Copyright © 1997 Elsevier Science Ltd. All rights reserved

Keywords: heat capacity, adiabatic calorimetry, zirconates.

1. INTRODUCTION

In case of a very severe nuclear reactor accident interactions of fission products with the zircaloy cladding (as well as the concrete basemat) are likely to occur. Formation of compounds during this interaction may greatly influence the release of less volatile but radiologically highly hazardous fission products, like the rare earth elements. For that reason better understanding of the energetics of compounds such as the light lanthanide zirconates, $\text{Ln}_2\text{Zr}_2\text{O}_7$, can enhance the accuracy of safety analyses for nuclear power plants.

Cerium zirconate $\text{Ce}_2\text{Zr}_2\text{O}_7$ (in the system Zr–Ce–O) is metastable at room temperature and will easily be oxidised to a solid solution of ZrO_2 and CeO_2 at temperatures above some 700 K [1, 2]. At elevated temperatures ($T > 1600 \text{ K}$), in reducing atmospheres, 3+ becomes the stable valence of cerium in cerium oxide–zirconium oxide mixtures [3–5]. Conditions typical for a severe nuclear reactor accident would be high temperatures (up to some 2600 K) and a reducing (hydrogen containing) atmosphere. $\text{Ce}_2\text{Zr}_2\text{O}_7$ is therefore the relevant oxidic cerium–zirconium compound for nuclear safety analysis purposes.

There is a considerable interest in rare earth zirconates because of possible applications as host materials for fluorescence centres [6], high-temperature heating elements, oxidation catalysts [7], fuel cell electrode materials [8] and the mentioned importance in nuclear safety analysis. Despite this interest comparatively few

data on their thermodynamic properties can be found. For this reason the thermodynamic functions of $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{Ce}_2\text{Zr}_2\text{O}_7$ have been determined from four to 1000 K. This has been done by adiabatic calorimetry for temperatures up to 400 K and drop calorimetry for temperatures between 500 and 900 K.

2. EXPERIMENTAL

2.1. Preparation of $\text{La}_2\text{Zr}_2\text{O}_7$

ZrO_2 (Aldrich, $\text{Hf} < 2 \cdot 10^{-4}$) was heated at 1473 K to remove adsorbed moisture. La_2O_3 was prepared by dissolving $\text{La}_2(\text{CO}_3)_3 \cdot 8 \text{H}_2\text{O}$ in nitric acid, and subsequently producing a precipitate by addition of NH_3 (aq) in excess. The precipitate was dried in air and then heated in oxygen at 1173 K to remove the nitrogen containing fragments. The resulting lanthanum oxide was heated at 1473 K to remove any absorbed water, and analyzed as 99.9% pure. After drying the starting materials were stored in an argon-filled glove box.

Lanthanum zirconate was prepared by thoroughly mixing stoichiometric amounts of the constituent oxides. The mixture was uniaxially pressed to pellets and sintered in platinum boats under purified argon at 1773 K for 10 hrs. After heating and thoroughly grinding, the sample's phase composition was checked by X-ray diffraction. This procedure was repeated several times to obtain pure $\text{La}_2\text{Zr}_2\text{O}_7$. The final X-ray pattern (Guinier–de Wolff, $\text{Cu K}\alpha_{1,2}$) made it possible to

determine the lattice symmetry as cubic, with lattice parameter 1.080 42 nm and space group F23 (196) [9]. So the structure of this zirconate is probably a slightly distorted pyrochlore, having lower symmetry than a true pyrochlore (space group Fd3m (227)).

2.2. Preparation $Ce_2Zr_2O_7$

The preparation of $Ce_2Zr_2O_7$ was comparable to the route taken for $La_2Zr_2O_7$. An accurately known quantity of dry ZrO_2 was introduced in a platinum beaker. A stoichiometric amount of an acidic $Ce(NO_3)_3$ (Merck, extra pure) solution of precisely known Ce-concentration (approximately 15 wt% Ce) was added to the ZrO_2 , and subsequently a precipitate was produced by adding NH_3 in excess. The precipitate-containing ZrO_2 was dried in air and then heated in air at 1173 K to remove the nitrogen containing fragments.

The resulting stoichiometric mixture of ZrO_2 and CeO_2 was further homogenised with pestle and mortar. The powder was uniaxially pressed to pellets and sintered in platinum boats under purified argon at 1823 K for 8 hrs, then switching to argon + 5% hydrogen for two additional hours at the same temperature. The last atmosphere was also used during cooling to room temperature to prevent reoxidation of the sample. The hydrogen was used to facilitate the reduction of Ce^{4+} to Ce^{3+} [6, 10, 11]. After heating and thoroughly grinding in a zirconia ball mill, the sample's phase composition was checked by X-ray diffraction. This procedure was repeated several times to obtain pure $Ce_2Zr_2O_7$. The final X-ray pattern (Guinier-de Wolff, Cu $K_{-1,2}$) is nearly identical to that published by JCPDS [12]. The cerium zirconate appeared to be isostructural with $La_2Zr_2O_7$, the diffraction pattern indicating a cubic lattice symmetry. The lattice parameter is 1.05877(19) nm and space group F23 (196). A list of observed diffraction lines is given in Table 1.

2.3. Calorimetry

Measurements of the c_p° between 4 and 400 K were performed in a custom-built adiabatic calorimeter (version cal VII, a copy of cal V which was described elsewhere [13]). Deviations in measured heat capacities from the reference values for NBS (National Bureau of Standards, now known as NIST) standard reference material No. 720 (synthetic sapphire (Al_2O_3)) are smaller than 0.1% over the whole temperature interval. The experimental determination of the heat capacity was performed on samples of $Ce_2Zr_2O_7$ or $La_2Zr_2O_7$ weighing approximately 18 g.

The enthalpy increments above room temperature were measured in an isothermal diphenyl-ether calorimeter which was described previously [14]. The

Table 1. X-ray diffraction data of $Ce_2Zr_2O_7$

$d_{obs}/\text{\AA}$	$d_{calc}/\text{\AA}$	hkl	I_{est}
6.103	6.113	1 1 1	20
5.282	5.294	2 0 0	5
3.736	3.743	2 2 0	20
3.186	3.192	3 1 1	10
3.058	3.056	2 2 2	100
2.648	2.647	4 0 0	60
2.430	2.429	3 3 1	< 5
2.364	2.368	4 2 0	< 5
2.161	2.161	4 2 2	< 5
2.036	2.038	3 3 3	< 5
1.872	1.872	4 4 0	70
1.597	1.596	6 2 2	80
1.529	1.528	4 4 4	40

CuK α , λ : 1.540 598 \AA int.std α - SiO_2 sys: Cubic S.G.: F23 (196) a: 10.5877(19) \AA Z: 8 ρ_x : 6.43 $g \cdot cm^{-3}$
Figure of merit: F(13) = 26 (0.0293, 17)

sample is enclosed in a high purity silver ampoule (spherical, 20 mm in diameter and 0.25 mm wall thickness). The (filled) ampoule is heated to a temperature known to 0.1 K. After ample equilibration time, the container is dropped into the calorimeter. The energy of the silver ampoule plus the sample contained therein then melts the diphenyl ether, in equilibrium with its liquid in a closed system. The resulting volume increment is determined by weighing the displaced mercury. The calorimeter is calibrated against NBS standard reference material No. 720. The calibration results agree within 0.2% with the data given by the National Bureau of Standards. The enthalpy contributions of the silver ampoules were determined separately [15].

3. THE ENTHALPIES OF FORMATION OF $Ln_2Zr_2O_7$

The enthalpy of formation of $La_2Zr_2O_7$ has been determined by high-temperature solution calorimetry [9]. On trying to measure the enthalpy of formation of $Ce_2Zr_2O_7$ with the same technique, it appeared that the $Ce_2Zr_2O_7$ would oxidize to CeO_2-ZrO_2 in the atmosphere of the calorimeter. This was probably due to the oxygen potential of the solvent (molten $Pb_2B_2O_5$ at 974 K), because the oxidation could not be prevented by flushing (± 25 ml/min) the calorimeter with purified argon (passed through Ti-filter at 1250 K). To be able to present a complete $\Delta_f G^\circ$ function for $Ce_2Zr_2O_7$ it is necessary to obtain a $\Delta_f H^\circ$ value. The enthalpies of formation for a series of lanthanide zirconates were measured by Korneev *et al.* [16]. They did however not arrive at $Ce_2Zr_2O_7$ but at $Ce_2Zr_2O_{7+x}$ (i.e. most Ce is 4+). So the enthalpy of formation measured by Korneev is not useful for our purpose. Therefore, an attempt has been made to

Table 2. Enthalpies of formation from constituent oxides (in kJ/mol) as measured by Korneev *et al.* [16] and an estimate thereof based on interatomic distances Ln–O

	$\Delta_f H_{\text{Korneev}}^\circ$ (kJ · mol ⁻¹)	$\Delta_f H^\circ(1/d_{\text{Ln-O}})$ (kJ · mol ⁻¹)
$\text{La}_2\text{O}_3 + 2 \text{ZrO}_2 - \text{La}_2\text{Zr}_2\text{O}_7$	-125.9	-125.2
$\text{Ce}_2\text{O}_3 + 2 \text{ZrO}_2 - \text{Ce}_2\text{Zr}_2\text{O}_7$		-121.1
$\text{Pr}_2\text{O}_3 + 2 \text{ZrO}_2 - \text{Pr}_2\text{Zr}_2\text{O}_7$		-117.0
$\text{Nd}_2\text{O}_3 + 2 \text{ZrO}_2 - \text{Nd}_2\text{Zr}_2\text{O}_7$	-110.9	-112.9
$\text{Pm}_2\text{O}_3 + 2 \text{ZrO}_2 - \text{Pm}_2\text{Zr}_2\text{O}_7$		-112.9
$\text{Sm}_2\text{O}_3 + 2 \text{ZrO}_2 - \text{Sm}_2\text{Zr}_2\text{O}_7$	-106.7	-105.4

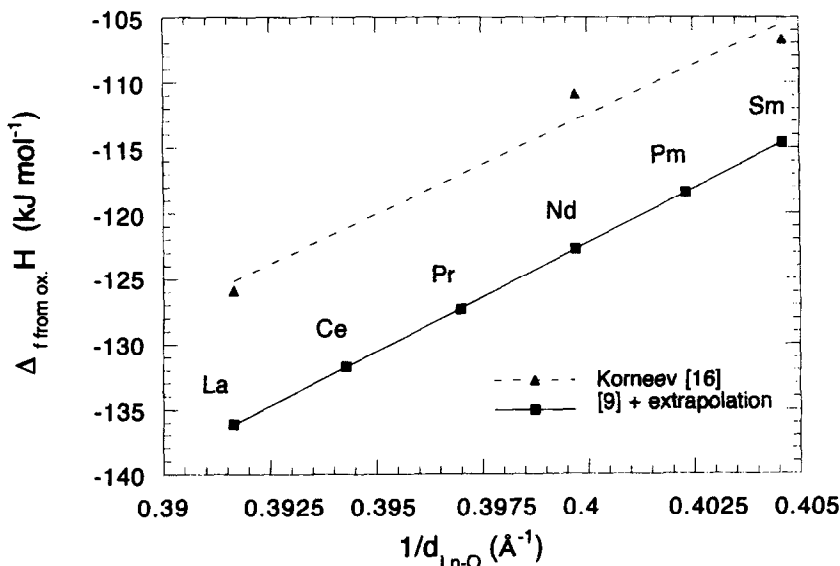


Fig. 1. Enthalpies of formation of $\text{Ln}_2\text{Zr}_2\text{O}_7$ from the constituent oxides ($\text{Ln}_2\text{O}_3 + 2\text{ZrO}_2 \rightarrow \text{Ln}_2\text{Zr}_2\text{O}_7$) for the light lanthanides (Ln), as a function of $1/(\text{sum of radii of } \text{Ln}^{3+} \text{ and } \text{O}^{2-})$. The specific kind of $\text{Ln}_2\text{Zr}_2\text{O}_7$ is indicated in the figure with the element symbol for the lanthanide. The data are taken from Korneev *et al.* [16], Bolech *et al.* [9] and an extrapolation thereof.

'extrapolate' the value obtained for the enthalpy of formation of $\text{La}_2\text{Zr}_2\text{O}_7$ to the corresponding enthalpies of formation for smaller lanthanide zirconates.

Because in the formation-reactions for La-, Nd- and Sm-zirconate (as measured by Korneev *et al.* [16]), the respective starting oxides and reaction products are isostructural, a linear relation between the enthalpy of formation-reaction and the reciprocal distance Ln–O may be presumed. Linear regression produces a relation between the enthalpy of reaction

from the oxides and $1/d_{\text{Ln-O}}$:

$$\Delta_f H(1/d_{\text{Ln-O}}) = \{1522.1 \cdot (d_{\text{Ln-O}})^{-1} - 724.4\} \text{ kJ} \cdot \text{mol}^{-1} \quad (1)$$

where

$$d_{\text{Ln-O}} = r_{\text{Ln}} + r_{\text{O}} \quad (2)$$

Given Ln–O distances are the sum of the effective ionic radii, as reported by Shannon [17] for the

Table 3. Enthalpies of formation of the light lanthanide zirconates from their constituent oxides, extrapolated from that of $\text{La}_2\text{Zr}_2\text{O}_7$

	$\Delta(d_{\text{Ln-O}}/\text{Å})^{-1}$	$\Delta(\Delta_f H^\circ)/(\text{kJ} \cdot \text{mol}^{-1})$	$\Delta_f \text{ from ox } H^\circ/(\text{kJ} \cdot \text{mol}^{-1})$
$\text{La}_2\text{Zr}_2\text{O}_7$			-136.1 ± 6.4
$\text{Ce}_2\text{Zr}_2\text{O}_7$	0.00265	4.4 ± 0.8	-131.7 ± 6.5
$\text{Pr}_2\text{Zr}_2\text{O}_7$	0.00534	8.8 ± 1.6	-127.3 ± 6.6
$\text{Nd}_2\text{Zr}_2\text{O}_7$	0.00807	13.4 ± 2.4	-122.7 ± 6.8
$\text{Pm}_2\text{Zr}_2\text{O}_7$	0.01067	17.7 ± 3.1	-118.4 ± 7.1
$\text{Sm}_2\text{Zr}_2\text{O}_7$	0.01297	21.5 ± 3.8	-114.6 ± 7.4

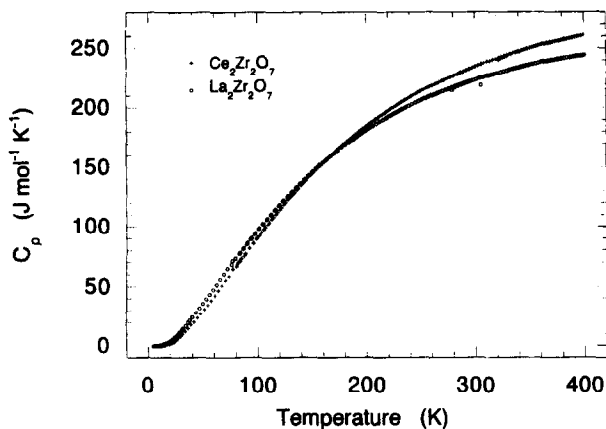


Fig. 2. Low-temperature heat capacity data for $\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Zr}_2\text{O}_7$.

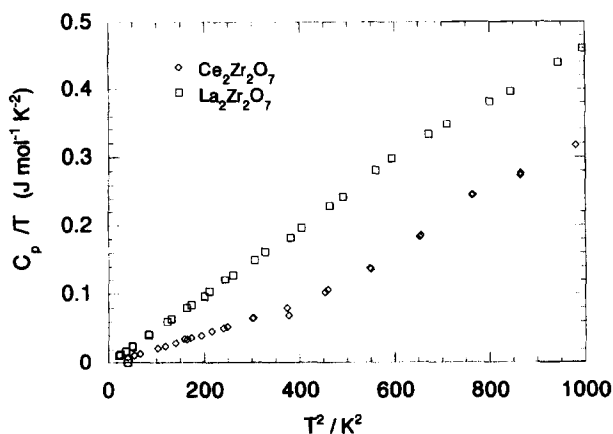


Fig. 3. Low-temperature heat capacity data, plotted in the form c_p/T vs T^2 , for temperatures below approximately 32 K. The heat capacity of $\text{Ce}_2\text{Zr}_2\text{O}_7$ being lower than that for $\text{La}_2\text{Zr}_2\text{O}_7$ is not what would be expected theoretically. This is probably due to lattice-defects introduced during preparation that cause a residual entropy.

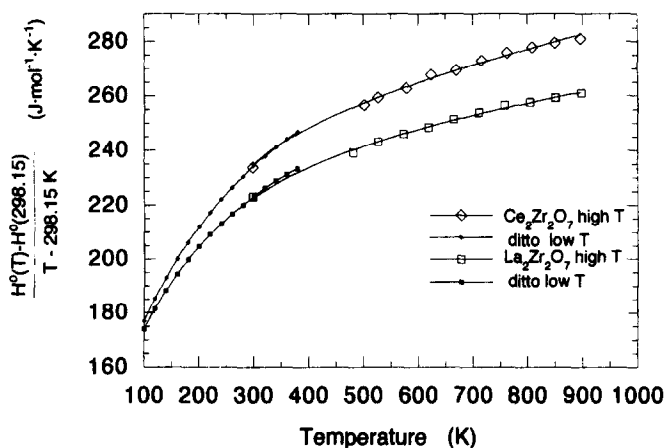


Fig. 4. The reduced enthalpy increments of $\text{Ce}_2\text{Zr}_2\text{O}_7$ and $\text{La}_2\text{Zr}_2\text{O}_7$ as a function of temperature. The high-temperature data are taken from enthalpy increment measurements (Table 6) and the low-temperature data are selected data from c_p measurements in an adiabatic calorimeter (Tables 4 and 5).

Table 4. Thermodynamic functions of Ce₂Zr₂O₇

<i>T</i> (K)	<i>c_p^o</i> (J/mol · K)	<i>S^o</i> (J/mol · K)	<i>H^o - H^o(0)</i> (J/mol)	$-\{G^o - H^o(0)\}/T$ (J/mol · K)
20	1.493	0.5733	8.6	0.1433
30	8.782	2.373	55.45	0.5243
40	18.88	6.237	192.3	1.431
50	30.00	11.57	433.4	2.902
60	42.15	18.10	793.5	4.877
70	54.60	25.53	1277	7.288
80	66.92	33.61	1884	10.07
90	79.31	42.23	2616	13.10
100	91.34	51.21	3470	16.51
110	102.85	60.44	4440	20.08
120	114.08	69.87	5524	23.84
130	124.78	79.43	6719	27.75
140	135.04	89.06	8019	31.78
150	144.71	98.71	9418	35.92
160	153.89	108.35	10,912	40.15
170	162.36	117.93	12,493	44.44
180	170.71	127.45	14,159	48.79
190	178.07	136.87	15,903	53.10
200	185.05	146.19	17,719	57.60
210	191.81	155.38	19,604	62.03
220	197.71	164.44	21,551	66.48
230	203.61	173.36	23,558	70.94
240	208.91	182.14	25,621	75.39
250	213.83	190.77	27,735	79.83
260	218.33	199.25	29,897	84.26
270	222.69	207.57	32,102	88.67
280	226.82	215.74	34,350	93.07
290	230.80	223.77	36,638	97.44
298.15	233.74	230.21	38,531	100.98
300	234.59	231.66	38,965	101.78
320	241.44	247.03	43,728	110.38
340	247.82	261.86	48,622	118.86
360	253.16	276.17	53,630	127.20
380	257.50	289.98	58,738	135.41

<i>T</i> (K)	<i>c_p^o</i> (J/mol · K)	<i>S^o</i> (J/mol · K)	<i>H^o - H^o(298)</i> (J/mol)	$-\{G^o - H^o(298)\}/T$ (J/mol · K)	$\Delta_r H^o$ (J/mol)	$\Delta_r G^o$ (J/mol)
298.15	233.74	230.21	0	230.21	-4,133,800	-3,923,187
300	234.59	231.66	434	230.21	-4,133,749	-3,921,877
400	260.00	303.01	25,295	239.77	-4,130,212	-3,851,744
500	274.94	362.74	52,093	258.56	-4,125,475	-3,782,659
600	285.69	413.86	80,148	280.28	-4,120,346	-3,714,576
700	294.46	458.58	109,167	302.63	-4,115,089	-3,647,363
800	302.18	498.41	139,006	324.65	-4,109,796	-3,580,905
900	309.28	534.42	169,583	345.99	-4,104,506	-3,515,115
1000	316.00	567.35	200,850	366.51	-4,105,192	-3,449,901

coordination numbers in a pyrochlore structure [18]. The enthalpies of formation that could be estimated with the regression function are given in the right column of Table 2. The data are graphically represented in Fig. 1. The enthalpy of formation from oxides of lanthanum zirconate, determined by Bolech *et al.* [9] as 136.1 kJ · mol⁻¹, deviates from the estimate in Table 2 (125.2 kJ · mol⁻¹). Because Korneev used an oxygen bomb calorimeter, pyrochlore formation may have been incomplete (glassy phases and lattice defects in the pyrochlore could have been produced without being noticed in the subsequent check with X-ray diffraction). Furthermore the error ($2 \cdot s_{\text{mean}}$) in the data of Korneev *et al.* (20 kJ · mol⁻¹) is about 3 times as large as the error in $\Delta_{\text{f from oxides}} H^o$ for

La₂Zr₂O₇ reported by Bolech *et al.* (6.4 kJ · mol⁻¹). Therefore this enthalpy of formation of La₂Zr₂O₇ was extrapolated, using the $d_{\text{Ln-O}}$ dependence of function 1 (from Korneev's data) multiplied by 136.1/125.2, to deduce the enthalpies of formation from oxides of Ln₂Zr₂O₇ according to:

$$\Delta(\Delta_r H^o) = \Delta(d_{\text{Ln-O}})^{-1} \cdot (1655 \pm 292) \text{ kJ} \cdot \text{mol}^{-1} \quad (3)$$

where

$$\Delta(\Delta_r H^o) = \Delta_{\text{f from ox}} H^o(\text{Ln}_2\text{Zr}_2\text{O}_7) - \Delta_{\text{f from ox}} H^o(\text{La}_2\text{Zr}_2\text{O}_7) \quad (4)$$

Table 5. Thermodynamic functions of $\text{La}_2\text{Zr}_2\text{O}_7$

T (K)	c_p° (J/mol · K)	S° (J/mol · K)	$H^\circ - H^\circ(0)$ (J/mol)	$-\{G^\circ - H^\circ(0)\}/T$ (J/mol · K)
20	3.892	1.315	19.72	0.3287
30	12.59	4.369	98.05	1.101
40	24.44	9.602	282.8	2.533
50	36.75	16.37	588.3	4.603
60	49.29	24.17	1018	7.202
70	61.87	32.72	1574	10.23
80	74.38	41.79	2255	13.60
90	86.03	51.22	3057	17.26
100	97.52	60.88	3975	21.14
110	108.41	70.69	5005	25.19
120	118.84	80.57	6141	29.40
130	128.34	90.46	7377	33.71
140	137.51	100.31	8707	38.12
150	146.19	110.10	10,126	42.59
160	154.60	119.81	11,630	47.12
170	161.92	129.40	13,213	51.67
180	169.37	138.87	14,870	56.26
190	175.64	148.18	16,593	60.85
200	181.94	157.35	18,380	65.45
210	187.54	166.35	20,227	70.04
220	192.60	175.19	22,127	74.62
230	197.61	183.87	24,078	79.18
240	202.06	192.37	26,077	83.72
250	206.24	200.71	28,118	88.23
260	210.13	208.87	30,200	92.71
270	213.87	216.87	32,320	97.17
280	217.14	224.71	34,475	101.58
290	220.26	232.38	36,663	105.96
298.15	223.05	238.53	38,470	109.50
300	223.41	239.91	38,883	110.30
320	229.12	254.53	43,413	118.86
340	234.03	268.56	48,045	127.26
360	238.41	282.06	52,769	135.48
380	241.55	295.05	57,571	143.54

T (K)	c_p° (J/mol · K)	S° (J/mol · K)	$H^\circ - H^\circ(298)$ (J/mol)	$-\{G^\circ - H^\circ(298)\}/T$ (J/mol · K)	$\Delta_f H^\circ$ (J/mol)	$\Delta_f G^\circ$ (J/mol)
298.15	223.05	238.53	0	238.53	-4,130,400	-3,930,437
300	223.41	239.91	413	238.53	-4,130,372	-3,929,194
400	243.45	307.25	23,869	247.58	-4,128,088	-3,862,441
500	255.42	362.95	48,851	265.25	-4,124,859	-3,796,391
600	264.26	410.33	74,852	285.58	-4,121,900	-3,730,972
700	271.63	451.63	101,655	306.41	-4,118,108	-3,666,119
800	278.22	488.34	129,152	326.90	-4,114,334	-3,601,804
900	284.35	521.47	157,284	346.71	-4,110,613	-3,537,964
1000	290.20	551.73	186,013	365.72	-4,106,941	-3,474,530

and

$$\Delta(d_{\text{Ln-O}})^{-1} = (r_{\text{Ln}} + r_{\text{O}})^{-1} - (r_{\text{La}} + r_{\text{O}})^{-1} \quad (5)$$

Using the method described, the following table of enthalpies of formation (from the constituent oxides) can be compiled.

4. RESULTS AND DISCUSSION

The low-temperature heat capacity measurements are shown in Figs 2 and 3. No phase transitions of any kind were observed for $\text{La}_2\text{Zr}_2\text{O}_7$ nor $\text{Ce}_2\text{Zr}_2\text{O}_7$. Smoothed thermodynamic functions were evaluated by extrapolating to 0 K and integrating. Values of the

functions at selected temperatures are given in Tables 4 and 5. For the very lowest temperatures the experimental heat capacity of cerium zirconate drops to lower values than would be expected (e.g. compared with $\text{La}_2\text{Zr}_2\text{O}_7$ or from a Debye extrapolation). This is probably due to residual entropy stemming from lattice defects introduced by sintering in a hydrogen containing atmosphere. The effect is small however, and probably can not be prevented because of the rapid oxidation of $\text{Ce}_2\text{Zr}_2\text{O}_7$ under atmospheres with traces of oxygen. Interestingly, this phenomenon was not observed for cerium silicate even though its preparation was done under argon plus 5% hydrogen too [19].

The high-temperature enthalpy increments are

Table 6. Enthalpy increments of La₂Zr₂O₇ and Ce₂Zr₂O₇

T/K	{H°(T) – H°(298.15)}/(J/mol)		
	exp.	calc.	Δ%
(a) Ce ₂ Zr ₂ O ₇			
500.7	51,990	52,286	–0.57
526.3	59,193	59,366	–0.29
577.8	73,489	73,829	–0.46
623.5	87,123	86,888	0.27
669.8	100,137	100,312	–0.17
715.8	114,022	113,830	0.17
762.2	127,977	127,637	0.27
808.0	141,658	141,426	0.16
849.6	154,076	154,083	0.00
896.4	168,140	168,470	–0.20
(b) La ₂ Zr ₂ O ₇			
480.8	43,684	43,966	–0.64
526.7	55,594	55,705	–0.20
573.0	67,633	67,746	–0.17
619.0	79,712	79,887	–0.22
665.3	92,313	92,271	0.05
711.2	104,837	104,701	0.13
757.7	117,884	117,440	0.38
803.7	130,229	130,182	0.04
850.2	143,106	143,198	–0.06
897.6	156,421	156,601	–0.12

listed in Table 6, and were fitted to obtain smoothed high temperature data. Boundary conditions for the fit were {H°(T) – H°(298.15)} = 0 at T = 298.15 K and c_p° at 298.15 K = value obtained from adiabatic calorimetry (as listed in Tables 4 and 5). For Ce₂Zr₂O₇ the following function was obtained (500–900 K):

$$H^{\circ}(T) - H^{\circ}(298.15) = \{4,078,234 \cdot (T/K)^{-1} + 262.4280 \cdot (T/K) + 0.02882741 \cdot (T/K)^2 - 94,483.9\} \text{ J/mol}$$

For La₂Zr₂O₇ the obtained function reads:

$$H^{\circ}(T) - H^{\circ}(298.15) = \{3,034,999.2 \cdot (T/K)^{-1} + 241.88260 \cdot (T/K) + 0.02567399 \cdot (T/K)^2 - 84,579.0\} \text{ J/mol}$$

The standard deviations in these fits are 282 J/mol for cerium zirconate and 222 J/mol in the case of lanthanum zirconate. The smoothed thermodynamic properties of cerium and lanthanum zirconate from

298.15 to 1000 K were derived from the given functions. For selected temperatures the values are given in the lower sections of Tables 4 and 5, respectively. The values for Δ_fH° and Δ_fG° have been calculated using the enthalpies of formation discussed before and data on the pure elements taken from the works of Cordfunke and Konings [20]. As can be seen in Fig. 4, the sets of data for low and high temperature measurements join smoothly at room temperature. As neither of the two zirconates were measured before, there are no literature values to compare.

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