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Thermochimica Acta 284 (1996) 253–261

thermochimica
acta

The heat capacity and derived thermodynamic functions of $La_2Si_2O_7$ and $Ce_2Si_2O_7$ from 4 to 1000 K

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Received 21 December 1995; accepted 5 January 1996

Abstract

The heat capacities of cerium and lanthanum silicates ($Ce_2Si_2O_7$ and $La_2Si_2O_7$) were measured from 4 to 400 K by adiabatic calorimetry. The derived thermodynamic functions, $\{H^\circ(T) - H^\circ(0)\}$, S° and $\{G^\circ - H^\circ(0)\}/T$ were calculated. The standard molar entropies at 298.15 K were determined as 220.32 ± 0.44 J mol^{-1} K^{-1} and 210.7 ± 0.42 J mol^{-1} K^{-1}, respectively.

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.

Keywords: Cerium silicate; Calorimetry; Entropy; Heat capacity; Lanthanum silicate

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1. Introduction

In a very severe nuclear reactor accident, interactions of fission products with the zircaloy cladding and the concrete basement are likely to occur. Formation of compounds during this interaction may greatly influence the release of less volatile but

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PII S0040-6031(96)02853-5

radiologically highly hazardous fission products, like the rare earth elements. For that reason better understanding of the thermodynamics of compounds such as the light lanthanide silicates, $Ln_2Si_2O_7$, can enhance the accuracy of safety analyses for nuclear power plants.

Cerium silicate $Ce_2Si_2O_7$ (in the system Si-Ce-O) is metastable at room temperature and can be oxidized to SiO_2 and CeO_2 at temperatures above *ca* 1100 K [1]. At elevated temperatures ($T > 1800$ K) 3 + becomes the stable valence of cerium in cerium oxide-silicon oxide mixtures, even in oxidizing atmospheres [2,3]. Furthermore, lanthanum and cerium silicates occur in two lattice varieties, a tetragonal low-temperature form and a monoclinic high-temperature form with a phase transition at approximately 1525 K [4,5].

Conditions typical for a severe nuclear reactor accident would be high temperatures (up to *ca* 2600 K) and a reducing (hydrogen-containing) atmosphere. The high-temperature modifications of $Ce_2Si_2O_7$ and $La_2Si_2O_7$ are, therefore, the relevant oxidized cerium-silicon compounds for nuclear safety analysis purposes.

All in all, there is a considerable interest in rare earth silicates [6] because of possible applications as host materials for fluorescence centres [7,8], high-temperature insulation material, crucible material for molten metals [9], 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 $La_2Si_2O_7$ and $Ce_2Si_2O_7$ have been determined from 4 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 $La_2Si_2O_7$

Dry La_2O_3 (weighted in an argon-filled glove box, purity better than 99.6 w%) was dissolved in nitric acid. To this solution a stoichiometric amount of TEOS (tetra ethyl orthosilicate, Merck selectipur, > 99 w%) plus an approximately equal volume of ethyl alcohol was added. Subsequently a gel was produced by addition of NH_3(aq) in excess. The precipate was dried in air and then heated in oxygen at 1173 K to remove organic and nitrogen-containing components. The resulting mixture was uniaxially pressed into pellets and sintered in platinum boats under purified argon at 1773 K for 10 h. After heating and thorough grinding the sample's phase composition was checked by X-ray diffraction. This procedure was repeated several times to obtain pure $La_2Si_2O_7$.

The final X-ray pattern (Guinier-de Wolff, $CuK_{\alpha_{1,2}}$ made it possible to determine the lattice symmetry as monoclinic, with lattice parameters $a = 13.1791(13)$Å, $b = 8.7934(10)$ Å, $c = 5.4099(7)$ Å, $\beta = 90.52^\circ$ and space group P21/n (14). These lattice characteristics are in good agreement with the extensive study of Felsche and co-workers [5,10,11] and a paper by Smolin and Shepelev [12]. The monoclinic character of the material leads to some confusion, however, which is apparent from the earliest publications just mentioned [10,12] in which the pyrosilicates are described as orthorhombic. Felsche later added the modifier 'pseudo-' to orthorhombic and also got the space group correct: P21/n (14) [5,11]. The magnitude of the monoclinic angle β that we determined as 90.52° is somewhat different from the 91.06° reported by Tas and Akinc [13]. Though exact interpretation of this difference is difficult due to typographic inaccuracies in the table of Tas and Akinc [13], the deviation seems real, with good reliability in the X-ray diffraction data. Both the set of data used in this work as well as that of Tas and Akinc have enough diffractions with negative indices and a good overall accuracy. The figure of merit [14] of our indexing of the diffraction pattern is $F_{26} = 73$ (0.0089,40).

2.2. *Preparation of* $Ce_2Si_2O_7$

The preparation of $Ce_2Si_2O_7$ was comparable to the route taken for $La_2Si_2O_7$. An accurately known amount of an acidic $Ce(NO_3)_3$ (Merck, extra pure) solution of precisely known Ce concentration (approximately 15 wt% Ce) was placed in a platinum beaker. To this solution a stoichiometric amount of TEOS plus an approximately equal volume of ethyl alcohol was added. Subsequently, a gel was produced by addition of NH_3(aq) in excess. The precipitate was dried in air and then heated in air at 1173 K to remove the nitrogen-containing components.

The resulting stoichiometric mixture of SiO_2 and CeO_2 was further homogenized with a pestle and mortar. The powder was uniaxially pressed into pellets and sintered in platinum boats under purified argon at 1823 K for 9.5 h, then switching to argon + 5% hydrogen for 30 min 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+} [1,3,4]. After heating and thorough grinding in a zirconia ball mill, the sample's phase composition was checked by X-ray diffraction. This procedure was repeated twice to obtain pure $Ce_2Si_2O_7$. The final X-ray pattern (Guinier–de Wolff, $CuK_{\alpha_{1,2}}$) is nearly identical to that published by Tas and Akinc [15]. The cerium silicate appeared to be isostructural with $La_2Si_2O_7$, the diffraction pattern indicating a monoclinic lattice symmetry. The lattice parameters are $a = 13.1147(30)$ Å, $b = 8.7508(20)$ Å, $c = 5.4173(13)$ Å, $\beta = 90.27°$ and space group P21/n (14). For cerium silicate there is a small difference between the indexed angle β and the 90.13 reported by Tas and Akinc [4].

2.3. *Calorimetry*

Measurements of the heat capacity 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 [16]). Deviations in measured heat capacities from the reference values for NBS (National Bureau of Standards, now 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 $Ce_2Si_2O_7$ or $La_2Si_2O_7$ weighing approximately 16 g.

The enthalpy increments above room temperature were measured in an isothermal diphenyl ether calorimeter which was described previously [17]. The 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 accurately known to within ± 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 to within ± 0.2% with the data given by the National Bureau of Standards. The enthalpy contributions of the silver ampoules were determined separately [18].

3. Results and discussion

The low-temperature heat capacity measurements are shown in Figs. 1 and 2. No phase transitions of any kind were observed for $Ce_2Si_2O_7$ nor $La_2Si_2O_7$. Smoothed thermodynamic functions were evaluated by extrapolating to 0 K and integrating. Values of the functions at selected temperatures are given in Tables 1 and 2.

The high-temperature enthalpy increments are listed in Table 3, and were fitted to obtain smoothed high-temperature data. Boundary conditions for the fit were $\{H^\circ(T) - H^\circ(298.15)\} = 0$ at $T = 298.15$ K and C_p° at 298.15 K = value obtained from

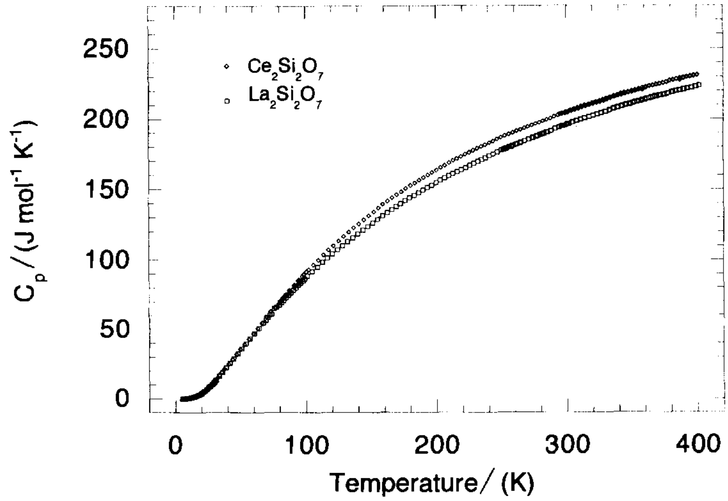

Fig. 1. Low-temperature heat capacity data for monoclinic $Ce_2Si_2O_7$ and $La_2Si_2O_7$.

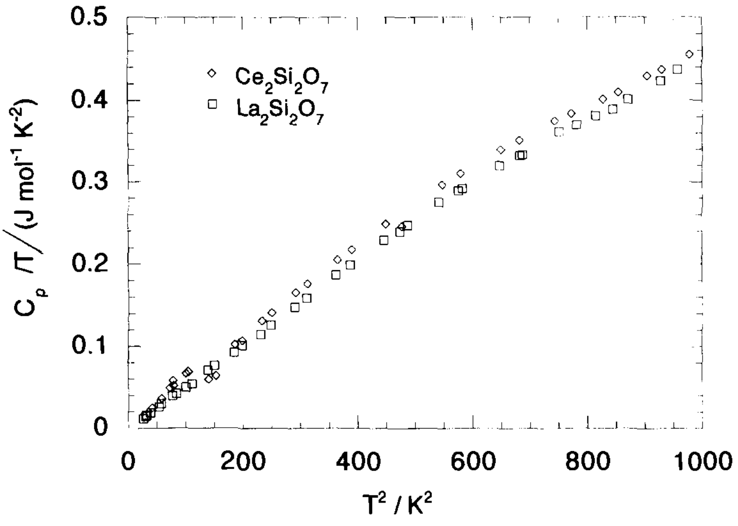

Fig. 2. Low-temperature heat capacity data, plotted in the form C_p/T versus T^2, for temperatures below approximately 32 K.

Table 1
Thermodynamic function of β-$Ce_2Si_2O_7$

T/K	C_p/ ($J\ mol^{-1}\ K^{-1}$)	S°/ ($J\ mol^{-1}\ K^{-1}$)	$H - H(0)$/ ($J\ mol^{-1}$)	$-\{G - H(0)\}/T$/ ($J\ mol^{-1}\ K^{-1}$)
20	4.474	1.405	21.08	0.3513
30	12.84	4.666	104.3	1.189
40	24.18	9.905	289.1	2.676
50	35.90	16.55	589.2	4.768
60	47.64	24.13	1007	7.353
70	59.21	32.35	1541	10.33
80	70.17	40.95	2186	13.62
90	80.68	49.84	2942	17.15
100	90.79	58.87	3800	20.87
110	100.28	67.97	4756	24.74
120	109.20	77.09	5804	28.72
130	117.60	86.16	6939	32.79
140	125.38	95.17	8154	36.92
150	132.77	104.07	9445	41.10
160	139.84	112.87	10809	45.31
170	146.25	121.54	12240	49.54
180	152.62	130.08	13734	53.78
190	158.22	138.48	15288	58.02
200	163.76	146.74	16898	62.25
210	168.98	154.85	18561	66.47
220	173.63	162.82	20275	70.67
230	178.34	170.65	22035	74.84

Table 1 (*Continued*)

T/K	C_p/ (J mol^{-1} K^{-1})	S°/ (J mol^{-1} K^{-1})	$H-H(0)$/ (J mol^{-1})	$-\{G-H(0)\}/T$/ (J mol^{-1} K^{-1})
240	182.66	178.33	23840	79.00
250	186.81	185.87	25687	83.12
260	190.73	193.27	27575	87.21
270	194.34	200.54	29501	91.28
280	198.10	207.68	31464	95.31
290	201.59	214.69	33462	99.30
298.15	204.41	220.32	35117	102.54
300	205.03	221.58	35496	103.27
320	211.44	235.03	39663	111.08
340	217.24	248.02	43950	118.76
360	222.53	260.59	48348	126.29
380	227.15	272.74	52844	133.68

T/K	C_p/ (J mol^{-1} K^{-1})	S°/ (J mol^{-1} K^{-1})	$H-H(298)$/ (J mol^{-1})	$-\{G-H(298)\}/T$/ (J mol^{-1} K^{-1})	$\Delta_f H$/ (J mol^{-1})	$\Delta_f G$/ (J mol^{-1})
298.15	204.41	220.32	0	220.32	−3807610	−3606195
300	205.03	221.58	379	220.32	−3807592	−3604941
400	230.39	284.41	22277	228.72	−3805936	−3537609
500	246.24	337.62	46154	245.32	−3803170	−3470829
600	258.36	383.63	71404	264.62	−3799910	−3404663
700	268.71	424.25	97768	284.58	−3796333	−3339066
800	278.13	460.75	125115	304.36	−3792491	−3274002
900	287.00	494.03	153375	323.61	−3788395	−3209437
1000	295.53	524.71	182504	342.20	−3790011	−3145331

Table 2

Thermodynamic functions of β-$La_2Si_2O_7$

T/K	C_p/ (J mol^{-1} K^{-1})	S°/ (J mol^{-1} K^{-1})	$H-H(0)$/ (J mol^{-1})	$-\{G-H(0)\}/T$/ (J mol^{-1} K^{-1})
20	4.119	1.357	20.36	0.339
30	12.38	4.452	99.42	1.138
40	23.54	9.542	279.0	2.567
50	35.13	16.04	572.2	4.593
60	46.57	23.45	980.8	7.108
70	57.56	31.47	1502	10.01
80	68.01	39.86	2132	13.21
90	77.86	48.44	2861	16.65
100	87.07	57.13	3686	20.26
110	95.75	65.83	4601	24.01
120	103.89	74.52	5600	27.86
130	111.54	83.14	6677	31.78

Table 2 (*Continued*)

T/K	C_p/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	S°/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$H-H(0)$/ ($\mathrm{J\,mol^{-1}}$)	$-\{G-H(0)\}/T$/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
140	118.73	91.67	7829	35.75
150	125.55	100.10	9051	39.76
160	132.09	108.41	10339	43.79
170	138.09	116.60	11690	47.84
180	144.14	124.67	13102	51.88
190	149.42	132.60	14569	55.92
200	154.79	140.40	16091	59.95
210	159.75	148.08	17664	63.97
220	164.31	155.62	19284	67.96
230	168.96	163.02	20951	71.93
240	173.28	170.31	22662	75.88
250	177.51	177.47	24416	79.80
260	181.26	184.50	26209	83.69
270	185.44	191.41	28042	87.56
280	188.78	198.21	29911	91.39
290	192.55	204.90	31817	95.19
298.15	195.18	210.27	33398	98.26
300	195.94	211.48	33759	98.95
320	201.62	224.31	37735	106.39
340	208.19	236.74	41836	113.69
360	213.97	248.80	46055	120.87
380	218.77	260.49	50381	127.91

T/K	C_p/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	S°/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$H-H(298)$/ ($\mathrm{J\,mol^{-1}}$)	$-\{G-H(298)\}/T$/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)	$\Delta_f H$/ ($\mathrm{J\,mol^{-1}}$)	$\Delta_f G$/ ($\mathrm{J\,mol^{-1}\,K^{-1}}$)
298.15	195.18	210.27	0	210.27	−3815720	−3619478
300	195.94	211.48	361	210.28	−3815722	−3618259
400	223.46	272.03	21475	218.34	−3814699	−3552541
500	240.08	323.79	44704	234.39	−3812272	−3487260
600	252.40	368.70	69351	253.11	−3809731	−3422488
700	262.70	408.40	95118	272.51	−3805998	−3358237
800	271.90	444.09	121855	291.77	−3801945	−3294542
900	280.48	476.61	149478	310.52	−3797611	−3231377
1000	288.67	506.59	177938	328.65	−3793000	−3168705

adiabatic calorimetry. For $Ce_2Si_2O_7$ the following function was obtained (500 to 900 K):

$$H(T) - H(298.15) = \{3631886 \times (T/\mathrm{K})^{-1} + 222.3716 \times (T/\mathrm{K}) + 0.03839521 \times (T/\mathrm{K})^2 - 81894.6\}\ \mathrm{J\,mol^{-1}}$$

Table 3
Enthalpy increments of $Ce_2Si_2O_7$ and $La_2Si_2O_7$

	$\{H^\circ(T) - H^\circ(298.15)\}/(\text{J mol}^{-1})$		
T/K	Exp.	Calc.	Δ%
$Ce_2Si_2O_7$			
516.9	50064	50334	−0.54
547.3	57713	57946	−0.40
578.2	65850	65798	0.08
625.1	77839	77923	−0.11
671.4	90494	90123	0.41
717.2	102490	102404	0.08
763.3	114870	114970	−0.09
804.4	126429	126340	0.07
845.7	138002	137920	0.06
887.1	149474	149680	−0.14
919.3	158960	158931	0.02
$La_2Si_2O_7$			
516.6	48175	48708	−1.11
578.0	63602	63826	−0.35
624.2	75557	75492	−0.09
670.3	87480	87359	0.14
716.5	99475	99466	0.01
762.7	111771	111775	0.00
803.6	123282	122834	0.36
845.1	134368	134207	0.12
886.6	145620	145727	−0.07
928.3	157179	157449	−0.17

For $La_2Si_2O_7$ the obtained function reads:

$$H(T) - H(298.15) = \{4188070 \times (T/\text{K})^{-1} + 220.8150 \times (T/\text{K}) + 0.03601947 \times (T/\text{K})^2 - 83084.7\}\ \text{J mol}^{-1}$$

The standard deviations in these fits are 197 J mol^{-1} for cerium silicate and 288 J mol^{-1} for lanthanum silicate. The smoothed thermodynamic properties of cerium and lanthanum silicate 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 1 and 2, respectively. The values for $\Delta_f H^\circ$ and $\Delta_f G^\circ$ have been calculated using the enthalpies of formation from our own measurements [19] and data on the pure elements taken from the works of Cordfunke and Konings [20].

As can be seen in Fig. 3, the sets of data for low- and high-temperature measurements join smoothly at room temperature. As neither of the two silicates was measured before, there are no literature values to compare.

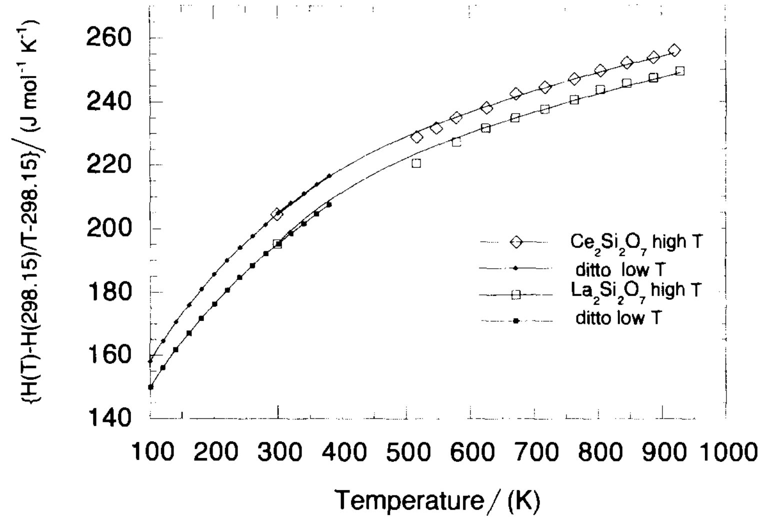

Fig. 3. The reduced enthalpy increments of monoclinic $Ce_2Si_2O_7$ and $La_2Si_2O_7$ as a function of temperature. The high-temperature data are taken from enthalpy increment measurements and the low-temperature data are deduced from C_p measurements in an adiabatic calorimeter.

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