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The heat capacity and derived thermophysical properties of $SrZrSi_2O_7$ from 5 to 1000 K

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Abstract

The low-temperature heat capacity of $SrZrSi_2O_7(s)$ was measured between 10 and 320 K by adiabatic calorimetry, and from the results the thermophysical properties $H^{\ominus}$, $S^{\ominus}$, and $[G^{\ominus} - H^{\ominus}(0)]/T$ were derived. For the standard molar entropy at 298.15 K, the value (190.14 ± 0.48) J mol^{-1} K^{-1} was found. Enthalpy increments relative to 298.15 K were measured by drop calorimetry from 400 to 850 K. The thermodynamic functions including the formation properties $\Delta_f H^{\ominus}(T)$ and $\Delta_f G^{\ominus}(T)$, were derived for temperatures up to 1000 K.

Keywords: Enthalpy increment; Entropy; Low-temperature heat capacity; $SrZrSi_2O_7$; Thermophysical properties

1. Introduction

In the unlikely event of a severe nuclear accident, the core of a nuclear reactor may melt through the reactor vessel and fall onto the concrete basemat underneath. Since under these circumstances the temperatures would be very high (> 1500 K), less volatile fission products, such as Ba, Ce, La, and Sr, may be released from the core-debris/concrete interaction.

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Knowledge of the thermodynamic properties of the compounds formed during these interactions enables us to calculate their release behaviour more accurately. In a previous study [1] the basic thermodynamic functions of strontium silicates in the binary system ($SrO-SiO_2$) were determined. In the ternary system $SrO-SiO_2-ZrO_2$ two pseudo-ternary oxides have been identified: $SrZrSi_2O_7$(s) and $Sr_6ZrSi_5O_{18}$(s) [2,3]. The thermodynamic properties of these compounds are completely unknown. In the present paper we present a combined study of the low-temperature heat capacity and the high-temperature enthalpy increments of $SrZrSi_2O_7$(s), from which the thermochemical properties have been derived, including the formation properties as functions of temperature.

2. Experimental

2.1. Preparation

$SrZrSi_2O_7$(s) was prepared in two separate steps using the TEOS-method as described previously by Ueno et al. [4]. In the first step $SrCO_3$(s) (Cerac, mass per cent 99.999) was dissolved gently in aqueous HNO_3 (1.8 mol dm^{-3}) and mixed with a calculated amount of TEOS (tetraethyl orthosilicate, Merck, mass per cent > 98). After adding an equal volume of ethyl alcohol (Merck, mass per cent > 99.8) the mixture was precipitated with concentrated NH_4OH. The sample was then dried in an oven (353 K) and decomposed in a gold boat in a stream of purified oxygen, at 1073 K. In the second step the calculated stoichiometric amount of ZrO_2(s) (Aldrich, mass per cent 99.995, <200 ppm Hf) was added to the mixture. The pure compound was obtained by heating the sample in a platinum boat in a purified argon atmosphere. After each heating the sample was ground in an alundum mortar and analysed by X-ray diffraction (Guinier de Wolff, Cu $K\alpha_{1,2}$). This sequence was repeated at gradually higher temperatures up to 1673 K until the sample was pure. To compensate for possible oxygen losses during these heatings the sample was finally heated in a gold boat in a purified oxygen atmosphere at 973 K.

Using this procedure two batches of $SrZrSi_2O_7$ were prepared (series 15 and 21). Crystallographic analyses indicated the sample of series 15 to be phase pure [5] whereas series 21 still contained 1 mol% of monoclinic ZrO_2 (JCPDS No. 37-1484). Since it was not possible to obtain accurate analytical results, no further efforts were made and only the molar ratios obtained from the masses of the starting

Table 1
Molar mass and molar ratio of $SrZrSi_2O_7$

Compound	M in g mol^{-1}	$n(SrO)/n(ZrO_2)$	$n(SiO_2)/n(ZrO_2)$
Sr(Zr,Si)-15-15	347.011	0.9993	2.0013
Sr(Zr,Si)-20-11		1.0000	2.0000

Table 2
The low-temperature molar heat capacities of $SrZrSi_2O_7(s)$ from 10 to 320 K

T in K	C_p° in J mol^{-1} K^{-1}	T in K	C_p° in J mol^{-1} K^{-1}	T in K	C_p° in J mol^{-1} K^{-1}
10.22	0.169	56.26	34.67	184.32	137.77
10.29	0.187	59.50	37.99	188.29	139.99
11.51	0.341	62.81	41.36	192.24	142.09
11.68	0.406	66.17	44.74	196.15	144.17
12.91	0.557	69.59	48.18	200.02	146.27
13.22	0.575	72.98	51.82	203.86	148.32
14.51	0.873	76.24	54.60	207.67	150.23
14.93	1.04	79.35	57.80	211.46	152.05
16.08	1.29	82.31	60.61	215.22	153.91
16.52	1.42	85.16	63.39	218.95	155.74
17.76	1.85	87.92	65.91	222.66	157.55
18.27	2.03	90.44	68.51	226.34	159.31
19.59	2.50	90.59	68.41	230.00	160.98
20.17	2.81	93.19	70.21	233.64	162.71
21.52	3.45	94.16	71.81	237.26	164.29
22.12	3.71	95.72	72.88	240.86	165.86
23.53	4.54	97.87	75.11	244.44	167.78
24.15	4.91	98.19	75.13	248.00	168.92
25.45	5.69	100.61	77.18	251.54	170.56
26.03	6.06	101.64	78.27	255.07	172.14
27.08	6.74	105.42	81.83	258.58	173.36
27.57	7.01	109.22	85.09	262.06	174.82
28.48	7.74	113.05	88.32	265.52	175.48
28.91	7.98	116.90	91.46	268.97	177.41
29.72	8.49	120.78	94.69	272.41	178.85
30.10	8.75	124.67	97.67	275.83	179.97
30.83	9.31	128.57	100.67	279.24	181.34
31.18	9.55	132.49	103.68	282.63	182.64
32.16	10.11	136.42	106.60	286.01	183.80
33.08	10.88	140.36	109.38	289.38	185.02
33.36	11.29	144.31	112.32	292.74	186.24
33.94	11.85	148.28	115.02	296.08	187.34
34.74	12.39	152.25	117.88	299.42	188.44
35.98	14.42	156.24	120.63	302.74	189.61
38.49	16.91	160.23	123.17	306.05	190.51
41.22	19.58	164.23	125.75	309.36	191.53
44.06	22.31	168.24	128.34	312.66	192.61
46.99	25.23	172.25	130.70	315.95	193.68
45.00	28.30	176.28	133.09	319.23	194.72
53.09	31.47	180.30	135.43		

materials were calculated (Table 1). The low-temperature heat capacity measurements were performed with a mixture of both batches. The experimental and smoothed values listed in Tables 1 and 2 are not corrected for the heat capacity of

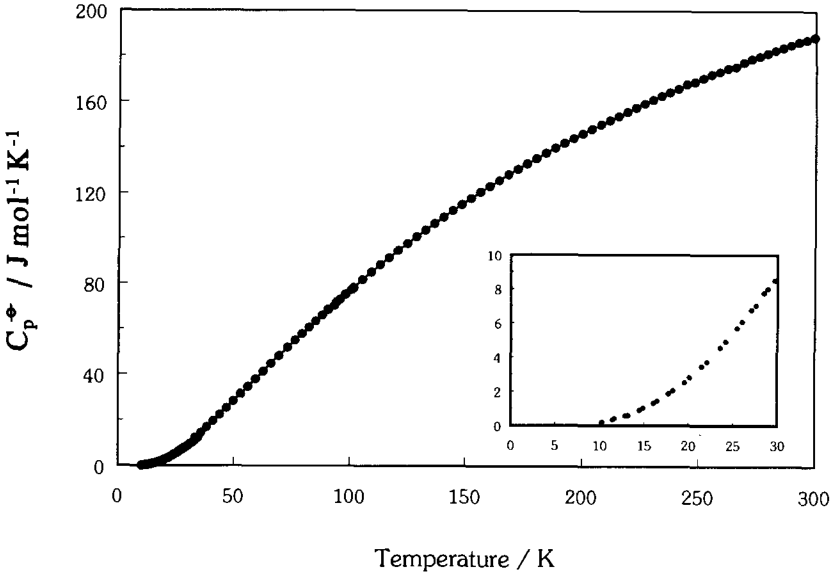

Fig. 1. The experimental low-temperature molar heat capacity of $SrZrSi_2O_7(s)$ from 0 to 300 K; the low-temperature region is shown in the insert.

ZrO_2 (0.37 mol%). The sample used for the enthalpy-increment measurements contained no zirconia.

2.2. Calorimetric techniques

The low-temperature heat capacities were measured in an adiabatic calorimeter (laboratory designation CAL V) over the temperature range 10–319 K. The calorimeter and its calibration have been described previously [6]. The temperature of the sample was measured with a 100 Ω platinum thermometer (Minco encapsulated type, calibrated Oxford Instruments against IPTS-68). For the measurement 13.6491 g or 39.333×10^{-3} mol of $SrZrSi_2O_7(s)$ was loaded into the calorimeter. To facilitate thermal contact between the sample and the calorimeter, helium at 1.0 kPa (300 K) was added after evacuation.

The enthalpy increments above 298.15 K were measured in an isothermal diphenyl ether drop calorimeter, which is a modified version of the Bunsen-type ice calorimeter, and has been described previously [7]. For the measurements, the sample was enclosed in spherical high-purity silver ampoule (20 mm diameter, 4.2 cm^3 volume) with a wall thickness of 0.25 mm. The ampoule was heated in a three-zone furnace, the temperature of which was measured with a calibrated Pt/(Pt10%Rh) thermocouple to 0.1 K. After thermal equilibration the ampoule was dropped into the calorimeter; the energy of the ampoule plus sample melts solid diphenyl ether in equilibrium with its liquid in a closed system. The resulting

Table 3
Thermodynamic properties at selected temperatures for $SrZrSi_2O_7$(s)

T in K	C_p° in J mol^{-1} K^{-1}	$S^\circ(T)-S^\circ(0)$ in J mol^{-1} K^{-1}	$H^\circ(T)-H^\circ(0)$ in J mol^{-1}	$-[G^\circ(T)-H^\circ(0)]/T$ in J mol^{-1} K^{-1}
10	0.251	0.0837	0.628	0.0216
20	2.716	0.7973	12.29	0.1829
30	8.678	2.952	67.44	0.7037
40	18.39	6.684	199.61	1.694
50	28.30	11.84	432.43	3.190
60	38.49	17.90	766.39	5.126
70	48.61	24.59	1202	7.423
80	58.41	31.75	1739	10.01
90	68.09	39.18	2371	12.84
100	76.59	46.78	3093	15.85
110	85.75	54.53	3907	19.01
120	94.07	62.35	4806	22.30
130	101.77	70.18	5785	25.68
140	109.12	78.00	6840	29.14
150	116.26	85.77	7968	32.66
160	123.02	93.50	9165	36.22
170	129.39	101.15	10427	39.81
180	135.25	108.71	11751	43.43
190	140.90	116.18	13132	47.06
200	146.26	123.54	14568	50.70
210	151.34	130.80	16056	54.35
220	156.25	137.96	17594	57.98
230	160.98	145.01	19181	61.61
240	165.48	151.96	20814	65.23
250	169.85	158.81	22491	68.84
260	173.94	165.55	24211	72.43
270	177.87	172.18	25968	76.00
280	181.64	178.72	27766	79.56
290	185.25	185.16	29600	83.09
298.15	188.02	190.33	31122	85.95
300	188.64	191.49	31470	86.59

volume increment of ether is determined by weighing the displaced mercury. The ratio of the heat input to the mass of mercury making up the volume increase is a constant for the apparatus, (79.9903 ± 0.0649) J g^{-1}, and is obtained by calibration with the NIST (formerly designated NBS) standard reference material No. 720, synthetic sapphire, Al_2O_3. Our results with sapphire all agree to within 0.2% with the data given by NIST. The enthalpy contribution of the silver ampoule was determined separately [8].

For this measurement, 4.44160 g of $SrZrSi_2O_7$(s) was enclosed in an ampoule of 4.41723 g. The loading of the ampoule was performed in an argon-filled glove box,

Table 4
Experimental and calculated molar enthalpy increments of $SrZrSi_2O_7(s)$

T in K	$[H^{\circ}(T)-H^{\circ}(298.15\ \text{K})]$ in J mol^{-1}		δ in %
	Exp.	Calc.	
485.4	39723	39790	−0.17
516.9	46925	47135	−0.45
517.1	46897	47182	−0.61
548.4	54533	54621	−0.16
578.0	61562	61777	−0.35
639.6	77229	77019	0.27
671.1	85350	84986	0.43
701.4	92909	92756	0.17
731.4	100681	100547	0.13
763.3	108749	108937	−0.17
794.5	117319	117245	0.06
825.9	125719	125708	0.01
855.2	133509	133694	−0.14

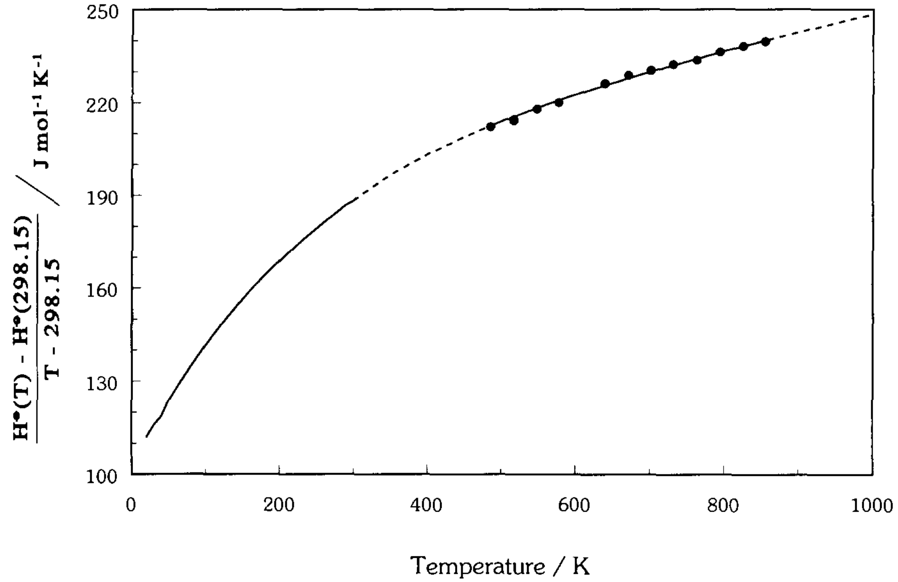

Fig. 2. The reduced enthalpy-increment function of $SrZrSi_2O_7(s)$ from 0 to 1000 K.

and all masses were corrected for buoyancy of argon. A correction was made for the difference in enthalpy between the final calorimeter temperature (300.06 K) and the standard reference temperature (298.15 K), using the value of C_p° obtained in this study.

Table 5
The smoothed high-temperature thermodynamic properties of $SrZrSi_2O_7(s)$ from 298.15 to 1000 K

T in K	$C_p^\ominus$ in J mol^{-1} K^{-1}	$S^\ominus$ in J mol^{-1} K^{-1}	$-[G-H(298)]/T$ in J mol^{-1} K^{-1}	$H(T)-H(298)$ in J mol^{-1}	$\Delta_f H^\ominus(T)$ in J mol^{-1}	$\Delta_f G^\ominus(T)$ in J mol^{-1}
298.15	187.810	190.140	190.140	0	−3640800	−3444018
300	188.498	191.304	190.144	348	−3640813	−3442796
400	215.726	249.642	197.913	20691	−3640506	−3376790
500	233.016	299.743	213.391	43176	−3638934	−3311024
600	246.394	343.448	231.502	67168	−3636618	−3245650
700	257.925	382.313	250.320	92394	−3633753	−3180711
800	268.472	417.450	269.050	118720	−3630390	−3116215
900	278.477	449.652	287.352	146070	−3627167	−3052098
1000	288.066	479.490	305.092	174398	−3622501	−2988444

3. Results and discussion

The experimental results of the low-temperature heat capacity measurement of $SrZrSi_2O_7(s)$ are listed in Table 2. No phase transitions have been observed (Fig. 1), although there is a small energy relaxation at 265 K. This is probably caused by internal stress of the sample; however, the contribution to the entropy will be negligible. Since the increment in the $C_p^\ominus$ values below is 13 K is very small no Debye function could be used; therefore an AT^3 fit, with $A = 2.51 \times 10^{-4}$ J mol^{-1} K^{-4}, was used for this temperature region. Interpolation and integration of the experimental data finally yielded the following values for the heat capacity and entropy at room temperature (Table 3)

$$C_p^\ominus(298.15\ \mathrm{K}) = (188.02 \pm 0.38)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$S^\ominus(298.15\ \mathrm{K}) = (190.33 \pm 0.48)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

and after correction for the zirconia impurity using data from Cordfunke and Konings [9]

$$C_p^\ominus(298.15\ \mathrm{K}) = (187.81 \pm 0.38)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

$$S^\ominus(298.15\ \mathrm{K}) = (190.14 \pm 0.48)\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

The high-temperature enthalpy increment measurements are given in Table 4. The high-temperature thermodynamic function was calculated by fitting the data to a polynomial with the boundary condition $[H^\ominus(T) - H^\ominus(298.15)] = 0$ at 298.15 K, and using the corrected $C_p^\ominus(298.15\ \mathrm{K})$ obtained in this study. For $SrZrSi_2O_7(s)$ we thus obtain from 298.15 to 855.2 K

$$\{H^\ominus(T) - H^\ominus(298.15)\}/\mathrm{J\ mol^{-1}} = 204.6077(T/\mathrm{K}) + 43.63192 \times 10^{-3}(T/\mathrm{K})^2 + 38.06008 \times 10^5(T/\mathrm{K})^{-1} - 77647.8$$

The differences between the measured and calculated values are also listed in Table 4. As can be seen in Fig. 2, there is a smooth fit between the low- and high-temperature data. With the function derived in this study and the previously reported standard molar enthalpy of formation of $SrZrSi_2O_7$ [10], the smoothed thermodynamic properties of Table 5 have been calculated up to 1000 K.

Since no thermodynamic data were available, no comparison could be made with the literature.

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