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# THE HEAT CAPACITY AND DERIVED THERMOPHYSICAL PROPERTIES OF SOME ALKALINE EARTH SILICATES AND ZIRCONATES FROM 5 TO 1000 K—I. CRYSTALLINE $SrSiO_3$ AND $Sr_2SiO_4$

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**Abstract**—The heat capacities of $SrSiO_3$ and $Sr_2SiO_4$ were measured from 5 to 350 K by adiabatic calorimetry, and the derived thermophysical properties, $H^\circ$, $S^\circ$, and $\{G^\circ - H^\circ(0)\}/T$ were calculated. For the standard molar entropies at 298.15 K the values $(95.65 \pm 0.21)$ J mol$^{-1}$ K$^{-1}$ and $(155.44 \pm 0.25)$ J mol$^{-1}$ K$^{-1}$, respectively were found, Enthalpy increments relative to 298.15 K were measured by drop calorimetry for $SrSiO_3$ from 503.0 to 886.4 K and for $Sr_2SiO_4$ from 503.0 to 886.2 K.

The thermodynamic functions including the formation properties $\Delta_f H^\circ(T)$ and $\Delta_f G^\circ(T)$, were derived for temperatures up to 1000 K.

*Keywords:* $SrSiO_3$, $Sr_2SiO_4$, heat capacity, entropy.

## 1. INTRODUCTION

The silicates of strontium are of particular interest in studies on nuclear reactor safety. During nuclear fission the radiologically hazardous fission product strontium is formed which will probably be present in the fuel as $SrZrO_3$ [1, 2]. In a severe nuclear accident the core of the reactor will melt, and may interact with the underlying concrete base-mat. At these high temperatures it is likely that new compounds are formed upon reaction with the concrete—in particular, with the main constitutent silica. To predict which strontium silicates may be formed under these conditions it is necessary to know their basic thermodynamic properties. Unfortunately, these properties are inaccurately known—possibly because they are of little geothermal interest. Weller and Kelley [3] measured the low-temperature heat capacities from 51 to 300 K, but high-temperature heat capacities have not been measured.

In this paper we present a combined study of the low- and high-temperature heat capacities of $SrSiO_3$ and $Sr_2SiO_4$ from which their thermochemical properties have been derived.

## 2. EXPERIMENTAL

### 2.1. *Preparation*

$SrSiO_3$(s) and $Sr_2SiO_4$(s) were prepared by heating stoichiometric amounts of $Sr(NO_3)_2$, prepared from $SrCO_3$ (Cerac, mass per cent 99.999), and TEOS (tetraethyl orthosilicate, Merck, mass per cent >98) after decomposition in a gold boat in oxygen at 975 K, according to Ueno *et al.* [4]. The reactions were completed at gradually increasing temperatures, up to 1775 K, in platinum boats, in a purified argon atmosphere. X-Ray powder diffraction (Guinier camera, Cu $K_\alpha$) showed the samples to be phase-pure. Si was analyzed by Inductively Coupled Plasm Atomic Emission Spectroscopy (ICP-AES) with an internal standard as reference; Sr was determined by complexometric titration with EDTA (Table 1).

### 2.2. *Calorimetric techniques*

The low-temperature heat capacities of $SrSiO_3$ and $Sr_2SiO_4$ were measured in an adiabatic calorimetric cryostat [5] (laboratory designation Mark XIII) over the temperature range 5–350 K, and are listed in Tables 2(a) and (b), respectively. A gold-plated, high-conductivity, oxygen free, copper calorimeter (laboratory designation W-99) was used. The calorimeter has a mass of 10.003 g and an internal volume of 10.0 cm$^3$. The temperature of the calorimeter was measured with a Leeds & Northrup encapsulated platinum resistance thermometer in an entrant well. The thermometer was calibrated by the U.S. National Bureau of Standards (now designated NIST) against IPTS-48 [6], and is considered to reproduce the thermodynamic temperature scale within 0.03 K from 5 to 300 K.

Table 1. Analytical results; molar mass and mass fraction *w*

| Compound | $M/(\mathrm{g\,mol^{-1}})$ | $10^2w(\mathrm{Sr})$ Found | $10^2w(\mathrm{Sr})$ Calc. | $10^2w(\mathrm{Si})$ Found | $10^2w(\mathrm{Si})$ Calc. |
|---|---|---|---|---|---|
| $SrSiO_3$ | 163.704 | $53.49 \pm 0.05$ | 53.52 | $17.15 \pm 0.06$ | 17.16 |
| $Sr_2SiO_4$ | 267.323 | $65.67 \pm 0.06$ | 65.55 | $10.52 \pm 0.33$ | 10.51 |

About 13.320 g of $SrSiO_3$ or 11.813 g of $Sr_2SiO_4$ were put into the calorimeter. The molar masses of $SrSiO_3$ and $Sr_2SiO_4$ are 163.70 and 267.32 $\mathrm{g\,mol^{-1}}$, respectively, based on the 1987 atomic masses. To facilitate rapid thermal equilibration 4.0 kPa at 297 K of helium gas were introduced into the calorimeter after evacuation. The calorimeter containing the sample was sealed in the inert atmosphere and then reopened on the vacuum line for the introduction of helium. The calorimeter was then sealed, placed in the cryostat, and cooled. The heat capacity of the empty calorimeter typically represented 70% of the total heat capacity at temperatures below 50 K, and decreased between 60.3 and 50% at higher temperatures.

The enthalpy increments above 298.15 K were measured in an isothermal diphenyl-ether calorimeter which has been described previously [7]. The sample is enclosed in a spherical (20 mm diameter, 4.2 $\mathrm{cm^3}$ volume) high-purity silver ampoule with a 0.25 mm

Table 2. The molar heat capacities of $SrSiO_3$ and $Sr_2SiO_4$

|  | $T$ (K) | $C_p^\circ$ $(\mathrm{J\,mol^{-1}\,K^{-1}})$ | $T$ (K) | $C_p^\circ$ $(\mathrm{J\,mol^{-1}\,K^{-1}})$ | $T$ (K) | $C_p^\circ$ $(\mathrm{J\,mol^{-1}\,K^{-1}})$ | $T$ (K) | $C_p^\circ$ $(\mathrm{J\,mol^{-1}\,K^{-1}})$ |
|---|---|---|---|---|---|---|---|---|
| (a) $SrSiO_3$ | | | | | | | | |
| | 6.50 | 0.051 | 43.33 | 11.309 | 114.23 | 45.92 | 232.27 | 78.64 |
| | 7.92 | 0.081 | 45.65 | 12.663 | 119.35 | 47.76 | 238.24 | 79.88 |
| | 9.15 | 0.114 | 48.00 | 13.964 | 124.48 | 49.57 | 244.21 | 80.96 |
| | 10.21 | 0.146 | 50.36 | 15.360 | 129.62 | 51.33 | 250.18 | 82.07 |
| | 11.26 | 0.185 | 52.74 | 16.70 | 134.77 | 53.07 | 256.08 | 83.13 |
| | 12.40 | 0.237 | 55.32 | 18.08 | 140.14 | 54.85 | 262.01 | 83.98 |
| | 13.64 | 0.314 | 58.11 | 19.59 | 145.73 | 56.51 | 268.06 | 85.13 |
| | 14.87 | 0.416 | 60.88 | 21.44 | 151.34 | 58.47 | 274.08 | 86.04 |
| | 16.09 | 0.552 | 63.69 | 22.64 | 156.86 | 60.19 | 280.10 | 87.32 |
| | 70.40 | 0.743 | 66.52 | 24.26 | 162.42 | 61.95 | 285.98 | 87.91 |
| | 18.84 | 1.012 | 69.65 | 25.90 | 167.99 | 63.52 | 292.91 | 88.85 |
| | 20.26 | 1.334 | 73.07 | 27.70 | 173.68 | 65.14 | 297.87 | 89.48 |
| | 21.68 | 1.709 | 76.50 | 29.49 | 179.36 | 66.68 | 303.81 | 90.50 |
| | 24.70 | 2.615 | 79.94 | 31.25 | 185.00 | 68.17 | 309.75 | 91.50 |
| | 26.36 | 3.161 | 83.40 | 32.95 | 190.64 | 69.57 | 315.68 | 92.59 |
| | 27.99 | 3.731 | 87.15 | 34.74 | 196.40 | 71.90 | 321.64 | 93.71 |
| | 29.65 | 4.347 | 91.43 | 36.71 | 202.41 | 72.35 | 327.62 | 94.96 |
| | 33.16 | 5.966 | 95.90 | 38.68 | 208.38 | 73.68 | 333.37 | 96.43 |
| | 35.14 | 6.985 | 100.39 | 40.56 | 214.34 | 74.68 | 339.92 | 97.67 |
| | 37.12 | 8.005 | 104.88 | 42.37 | 220.27 | 76.21 | 346.13 | 98.98 |
| | 39.12 | 9.082 | 109.41 | 44.12 | 226.28 | 77.60 | | |
| | 41.15 | 10.065 | | | | | | |
| (b) $Sr_2SiO_4$ | | | | | | | | |
| | 6.76 | 0.160 | 38.93 | 16.51 | 109.14 | 72.20 | 220.06 | 117.99 |
| | 8.29 | 0.233 | 40.96 | 18.56 | 113.52 | 74.17 | 225.93 | 119.41 |
| | 9.22 | 0.280 | 43.16 | 20.38 | 118.41 | 77.36 | 231.84 | 120.90 |
| | 10.24 | 0.332 | 45.50 | 22.56 | 123.70 | 80.32 | 237.62 | 122.40 |
| | 11.36 | 0.401 | 47.85 | 24.88 | 129.04 | 82.95 | 249.35 | 125.76 |
| | 12.35 | 0.483 | 50.22 | 27.03 | 134.38 | 85.65 | 267.00 | 130.96 |
| | 13.55 | 0.626 | 52.61 | 29.29 | 139.73 | 88.33 | 272.91 | 132.46 |
| | 14.71 | 0.832 | 55.24 | 31.62 | 145.14 | 90.99 | 278.86 | 133.93 |
| | 15.84 | 1.065 | 58.11 | 34.46 | 150.70 | 93.70 | 284.91 | 135.14 |
| | 17.13 | 1.548 | 61.01 | 37.12 | 156.40 | 96.38 | 290.77 | 136.08 |
| | 18.55 | 2.163 | 63.92 | 39.73 | 162.12 | 99.01 | 296.54 | 136.81 |
| | 19.98 | 2.889 | 66.84 | 42.35 | 167.86 | 101.55 | 302.44 | 137.44 |
| | 21.41 | 3.679 | 70.02 | 44.97 | 173.57 | 103.93 | 308.34 | 138.06 |
| | 24.42 | 5.346 | 73.46 | 47.80 | 179.32 | 106.19 | 314.25 | 138.83 |
| | 26.07 | 6.251 | 80.35 | 53.20 | 185.06 | 108.27 | 320.13 | 139.85 |
| | 27.73 | 7.232 | 83.82 | 55.77 | 190.86 | 110.22 | 326.03 | 141.28 |
| | 29.42 | 8.391 | 87.42 | 58.37 | 196.61 | 111.96 | 331.94 | 143.15 |
| | 31.13 | 9.772 | 91.52 | 61.22 | 202.46 | 113.61 | 337.80 | 145.30 |
| | 32.94 | 11.368 | 95.91 | 64.13 | 208.30 | 115.23 | 343.70 | 147.48 |
| | 34.91 | 13.077 | 100.31 | 66.92 | 214.20 | 116.58 | 348.13 | 148.78 |
| | 36.91 | 14.735 | 104.70 | 69.61 | | | | |

Table 3a. Smoothed thermodynamic properties at selected temperatures for $SrSiO_3$

| $T$<br>(K) | $C_p^\circ$<br>($J\,mol^{-1}\,K^{-1}$) | $S^\circ(T)-S^\circ(0)$<br>($J\,mol^{-1}\,K^{-1}$) | $H^\circ(T)-H^\circ(0)$<br>($J\,mol^{-1}$) | $-\{G^\circ(T)-H^\circ(0)\}/T$<br>($J\,mol^{-1}\,K^{-1}$) |
|---|---|---|---|---|
| 5 | 0.026 | 0.009 | 0.035 | 0.002 |
| 10 | 0.139 | 0.057 | 0.411 | 0.016 |
| 15 | 0.429 | 0.157 | 1.693 | 0.044 |
| 20 | 1.272 | 0.379 | 5.645 | 0.097 |
| 25 | 2.711 | 0.810 | 15.433 | 0.192 |
| 30 | 4.512 | 1.456 | 33.302 | 0.346 |
| 35 | 6.908 | 2.325 | 61.62 | 0.564 |
| 40 | 9.461 | 3.415 | 102.58 | 0.850 |
| 45 | 12.309 | 4.689 | 156.81 | 1.204 |
| 50 | 15.16 | 6.135 | 225.58 | 1.624 |
| 60 | 20.67 | 9.388 | 404.82 | 2.641 |
| 70 | 26.09 | 12.983 | 638.7 | 3.858 |
| 80 | 31.28 | 16.81 | 925.8 | 5.236 |
| 90 | 36.07 | 20.77 | 1262.9 | 6.741 |
| 100 | 40.40 | 24.80 | 1645.6 | 8.346 |
| 110 | 44.35 | 28.84 | 2069.7 | 10.026 |
| 120 | 48.00 | 32.86 | 2531.6 | 11.761 |
| 130 | 51.46 | 36.84 | 3029.0 | 13.537 |
| 140 | 54.81 | 40.77 | 3560.4 | 15.34 |
| 150 | 58.04 | 44.67 | 4124.8 | 17.17 |
| 160 | 61.15 | 48.51 | 4720.9 | 19.01 |
| 170 | 64.10 | 52.31 | 5347 | 20.85 |
| 180 | 66.86 | 56.05 | 6000 | 22.71 |
| 190 | 69.42 | 59.74 | 6684 | 24.56 |
| 200 | 71.80 | 63.36 | 7390 | 26.41 |
| 210 | 74.40 | 66.92 | 8119 | 28.25 |
| 220 | 76.16 | 70.41 | 8870 | 30.09 |
| 230 | 78.20 | 73.84 | 9642 | 31.92 |
| 240 | 80.17 | 77.21 | 10,434 | 33.73 |
| 250 | 82.04 | 80.52 | 11,245 | 35.54 |
| 260 | 83.81 | 83.77 | 12,075 | 37.33 |
| 270 | 85.44 | 86.97 | 12,921 | 39.11 |
| 280 | 86.95 | 90.10 | 13,783 | 40.88 |
| 290 | 88.40 | 93.18 | 16,660 | 42.63 |
| 298.15 | 89.61 | 95.65 | 15,385 | 44.04 |
| 300 | 89.90 | 96.20 | 15,551 | 44.36 |
| 325 | 94.46 | 103.57 | 17,853 | 48.64 |
| 350 | 99.80 | 110.76 | 20,281 | 52.82 |

wall thickness. The ampoule is heated in a furnace the temperature of which is measured with calibrated Pt/(Pt + 10 mass per cent Rh) thermocouples to 0.1 K. After a reasonable thermal equilibration time, the ampule is dropped into the calorimeter; the energy of the ampoule plus sample now melts solid diphenyl-ether in equilibrium, with its liquid in a closed system. The resulting 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 change, is a constant for the apparatus, $(79.9903 \pm 0.0649)\ Jg^{-1}$, and is obtained by calibration with the NBS standard reference material No. 720, synthetic sapphire, $Al_2O_3$. Our results with sapphire all agree (within 0.2%) with the data given by NBS. The enthalpy contributions of the silver ampoule were determined separately [8].

For the present measurements 5.20487 g of $SrSiO_3$ and 4.72655 g $Sr_2SiO_4$ were enclosed in ampoules of 4.60654 g and 4.62860 g, respectively. All weights were corrected for buoyancy in argon. The results of the measurements, 14 for $SrSiO_3$ and 11 for $Sr_2SiO_4$, are listed in the Tables 3(a) and (b), respectively. 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 $C_p^\circ$ (298.15 K) from this study.

## 3. RESULTS

The low-temperature heat-capacity data are listed in Table 2 and are plotted in Fig. 1. No phase transitions of any order are observed for $SrSiO_3$ and $Sr_2SiO_4$. Smoothed thermodynamic functions at selected temperatures were evaluated by extrapolating the experimental heat-capacity curve to 0 K and by integrating (Table 3). The computer programs

Table 3b. Smoothed thermodynamic properties at selected temperatures for $Sr_2SiO_4$

| $T$ (K) | $C_p^\circ$ ($\text{J mol}^{-1}\,\text{K}^{-1}$) | $S^\circ(T) - S^\circ(0)$ ($\text{J mol}^{-1}\,\text{K}^{-1}$) | $H^\circ(T) - H^\circ(0)$ ($\text{J mol}^{-1}$) | $-\{G^\circ(T) - H^\circ(0)\}/T$ ($\text{J mol}^{-1}\,\text{K}^{-1}$) |
|---|---|---|---|---|
| 5 | 0.033 | 0.009 | 0.038 | 0.001 |
| 10 | 0.263 | 0.086 | 0.650 | 0.021 |
| 15 | 1.001 | 0.306 | 3.488 | 0.073 |
| 20 | 2.749 | 0.805 | 12.374 | 0.186 |
| 25 | 5.574 | 1.706 | 32.799 | 0.394 |
| 30 | 8.920 | 3.021 | 69.14 | 0.717 |
| 35 | 13.166 | 4.709 | 124.15 | 1.162 |
| 40 | 17.73 | 6.763 | 201.32 | 1.730 |
| 45 | 22.39 | 9.120 | 301.61 | 2.417 |
| 50 | 27.04 | 11.720 | 425.20 | 3.216 |
| 60 | 36.05 | 17.45 | 741.0 | 5.103 |
| 70 | 44.65 | 23.66 | 1144.5 | 7.306 |
| 80 | 52.49 | 30.13 | 1630.2 | 9.752 |
| 90 | 59.84 | 36.74 | 2192.3 | 12.383 |
| 100 | 66.64 | 43.40 | 2825.2 | 15.15 |
| 110 | 72.93 | 50.05 | 3523.4 | 18.02 |
| 120 | 78.84 | 56.65 | 4282.4 | 20.97 |
| 130 | 84.12 | 63.17 | 5097 | 23.96 |
| 140 | 89.09 | 69.59 | 5963 | 26.99 |
| 150 | 93.70 | 75.89 | 6878 | 30.04 |
| 160 | 97.99 | 82.08 | 7836 | 33.10 |
| 170 | 101.98 | 88.14 | 8836 | 36.16 |
| 180 | 105.71 | 94.08 | 9875 | 39.22 |
| 190 | 109.20 | 99.89 | 10,950 | 42.26 |
| 200 | 112.49 | 105.57 | 12,058 | 45.28 |
| 210 | 115.58 | 111.14 | 13,199 | 48.29 |
| 220 | 118.50 | 116.58 | 14,369 | 51.27 |
| 230 | 121.28 | 121.91 | 15,568 | 54.22 |
| 240 | 123.91 | 127.13 | 16,794 | 57.15 |
| 250 | 126.42 | 132.24 | 18,046 | 60.05 |
| 260 | 128.81 | 137.24 | 19,322 | 62.93 |
| 270 | 131.09 | 142.15 | 20,622 | 65.77 |
| 280 | 133.25 | 146.96 | 21,944 | 68.58 |
| 290 | 135.30 | 151.67 | 23,287 | 71.37 |
| 298.15 | 136.89 | 155.44 | 24,396 | 73.62 |
| 300 | 137.24 | 156.29 | 24,649 | 74.12 |
| 325 | 141.53 | 167.45 | 28,136 | 80.88 |
| 350 | 144.88 | 178.07 | 31,718 | 87.44 |

FIFTAB2 and $C_p$-fit were used for all integrations and evaluations of thermodynamic functions [9, 10], yielding at room temperature for $SrSiO_3$:

$$C_p^\circ(298.15\ \text{K}) = (89.61 \pm 0.25)\ \text{J mol}^{-1}\,\text{K}^{-1},$$

$$S^\circ(298.15\ \text{K}) = (95.65 \pm 0.21)\ \text{J mol}^{-1}\,\text{K}^{-1},$$

and for $Sr_2SiO_4$:

$$C_p^\circ(298.15\ \text{K}) = (136.89 \pm 0.30)\ \text{J mol}^{-1}\,\text{K}^{-1},$$

$$S^\circ(298.15\ \text{K}) = (155.44 \pm 0.25)\ \text{J mol}^{-1}\,\text{K}^{-1}.$$

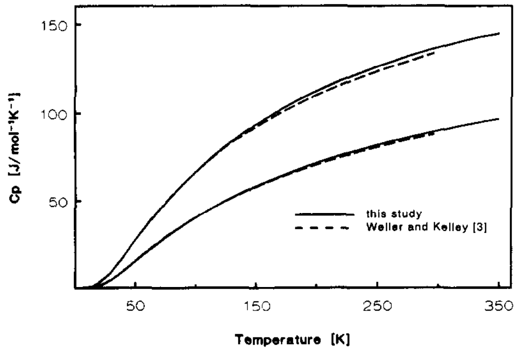

Fig. 1. The molar heat capacity of $SrSiO_3$ and $Sr_2SiO_4$.

The high-temperature enthalpy increments of $SrSiO_3$ are listed in Table 4, and were fitted to polynomials using as the boundary conditions $\{H^\circ(T) - H^\circ(298.15\ \text{K}\} = 0$ at 298.15 K, and $C_p^\circ(298.15\ \text{K} = (89.61 \pm 0.25)$ $\text{J mol}^{-1}$ $\text{K}^{-1}$. For $SrSiO_3$ we thus obtain (503.0–886.4 K):

$$\{H^\circ(T) - H^\circ(298.15\ \text{K})\}/\text{J mol}^{-1}$$

$$= 98.30627(T\,\text{K}^{-1}) + 16.27781 \times 10^{-3}(T\,\text{K}^{-1})^2$$

$$+ 16.35881 \times 10^5(T\,\text{K}^{-1})^{-1} - 36243.8.$$

The high-temperature enthalpy increments of $Sr_2SiO_4$ are also given in Table 4. In the literature two

Table 4. Enthalpy increments of $SrSiO_3$ and $Sr_2SiO_4$

| $T$ (K) | $\{H^\circ(T) - H^\circ(298.15\ K)\}/(J\ mol^{-1})$ Exp. | Calc. | $\delta$% |
|---|---|---|---|
| (a) $SrSiO_3$ | | | |
| 503.0 | 20,413 | 20,575 | −0.79 |
| 552.8 | 25,882 | 26,033 | −0.59 |
| 577.9 | 28,746 | 28,834 | −0.31 |
| 603.7 | 31,688 | 31,746 | −0.18 |
| 629.4 | 34,628 | 34,677 | −0.14 |
| 655.1 | 37,504 | 37,639 | −0.36 |
| 667.3 | 39,151 | 39,056 | 0.24 |
| 680.7 | 40,805 | 40,619 | 0.46 |
| 706.2 | 43,738 | 43,615 | 0.28 |
| 731.2 | 46,742 | 46,578 | 0.35 |
| 784.4 | 53,034 | 52,969 | 0.12 |
| 808.5 | 55,866 | 55,901 | −0.06 |
| 835.3 | 59,202 | 59,187 | 0.02 |
| 886.4 | 65,384 | 65,530 | −0.22 |
| (b) $Sr_2SiO_4$ | | | |
| 503.0 | 30,676 | 30,892 | −0.70 |
| 527.9 | 34,618 | 34,856 | −0.69 |
| 552.9 | 38,676 | 38,882 | −0.53 |
| 603.7 | 47,150 | 47,203 | −0.11 |
| 629.7 | 51,440 | 51,536 | −0.19 |
| 654.8 | 55,965 | 55,766 | 0.36 |
| 705.9 | 64,854 | 64,518 | 0.52 |
| 731.7 | 69,182 | 69,010 | 0.25 |
| 784.5 | 78,525 | 78,355 | 0.22 |
| 834.0 | 87,508 | 87,301 | 0.24 |
| 886.2 | 96.459 | 96.929 | −0.49 |

phase transitions for $Sr_2SiO_4$ have been reported. At 355 K monoclinic $\beta$-$Sr_2SiO_4$ (space group $P2_1/n$) transforms reversibly to $\alpha'$-$Sr_2SiO_4$ (space group *Pnmb*) with an enthalpy of transition of 213 J mol$^{-1}$ [11]. At about 775 K another reversible transition to the $\alpha$ phase is reported to occur [12]. This has been confirmed by high-temperature X-ray diffraction in this study. However, the enthalpy of this transition is too small to be measured in our DTA apparatus and will therefore be neglected in the calculations.

The enthalpy increment for the intermediate temperature region from 298.15 to 355 K, has been calculated by extrapolating and integrating the fit of the low-temperature heat capacity data. As usual the highest experimental points (above 325 K) have relatively large errors, and have therefore been omitted in

Table 5. The smoothed high-temperature thermodynamic properties of $SrSiO_3$ and $Sr_2SiO_4$ from 298.15 to 1000 K

| | $T$ (K) | $C_p^\circ$ (J mol$^{-1}$ K$^{-1}$) | $S^\circ$ (J mol$^{-1}$ K$^{-1}$) | $-(G^\circ - H^\circ(298))/T$ (J mol$^{-1}$ K$^{-1}$) | $H^\circ - H^\circ(298)$ (J mol$^{-1}$) | $\Delta_f H^\circ$ (J mol$^{-1}$) | $\Delta_f G^\circ$ (J mol$^{-1}$) |
|---|---|---|---|---|---|---|---|
| (a) $SrSiO_3$ | | | | | | | |
| | 298.15 | 89.610 | 95.650 | 95.650 | 0 | −1,635,300 | −1,549,903 |
| | 300 | 89.897 | 96.205 | 95.652 | 166 | −1,635,302 | −1,549,373 |
| | 400 | 101.104 | 123.766 | 99.333 | 9773 | −1,635,003 | −1,520,757 |
| | 500 | 108.041 | 147.117 | 106.616 | 20,251 | −1,634,242 | −1,492,276 |
| | 600 | 113.296 | 167.296 | 115.086 | 31,326 | −1,633,243 | −1,463,975 |
| | 700 | 117.757 | 185.103 | 123.841 | 42,884 | −1,632,084 | −1,435,854 |
| | 800 | 121.795 | 201.095 | 132.515 | 54,864 | −1,630,791 | −1,407,908 |
| | 900 | 125.587 | 215.661 | 140.956 | 67,235 | −1,629,995 | −1,380,061 |
| | 1000 | 129.226 | 229.082 | 149.106 | 79,976 | −1,628,115 | −1,352,388 |
| (b) $Sr_2SiO_4$ | | | | | | | |
| | 298.15 | 136.889 | 155.440 | 155.440 | 0 | −2,305,700 | −2,190,955 |
| | 300 | 137.239 | 156.288 | 155.443 | 254 | −2,305,692 | −2,190,244 |
| | 355.0 | 145.410 | 180.124 | 157.454 | 8048 | −2,305,332 | −2,169,593 |
| | 355.0 | 147.465 | 180.724 | 157.454 | 8261 | −2,305,119 | −2,169,593 |
| | 400 | 150.760 | 198.516 | 161.089 | 14,971 | −2,304,495 | −2,151,912 |
| | 500 | 158.082 | 232.944 | 172.118 | 30,413 | −2,303,128 | −2,113,920 |
| | 600 | 165.404 | 262.413 | 184.767 | 46,587 | −2,301,540 | −2,076,225 |
| | 700 | 172.727 | 288.460 | 197.754 | 63,494 | −2,299,694 | −2,038,816 |
| | 800 | 180.049 | 312.003 | 210.587 | 81,133 | −2,297,551 | −2,001,692 |
| | 900 | 187.372 | 333.632 | 223.072 | 99,504 | −2,296,332 | −1,964,712 |
| | 1000 | 194.694 | 353.753 | 235.146 | 118,607 | −2,292,855 | −1,928,045 |

the calculations. Thus, for $\beta$-$Sr_2SiO_4$ we obtain for 298.15–355 K:

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}}$$
$$= -37.3652(T\ \mathrm{K^{-1}}) + 75.6378 \times 10^{-2}(T\ \mathrm{K^{-1}})^2$$
$$-1.99360 \times 10^{-3}(T\ \mathrm{K^{-1}})^3$$
$$+3.30362 \times 10^{-6}(T\ \mathrm{K^{-1}})^4$$
$$-2.41484 \times 10^{-9}(T\ \mathrm{K^{-1}})^5$$
$$-53.4461 \times 10^2(T\ \mathrm{K^{-1}})^{-1} - 23657.1.$$

Using this polynomial the boundary condition for the high-temperature enthalpy increment of $\alpha'$-$Sr_2SiO_4$ is calculated to be 8261 J at 355 K. We thus obtain, for the $\alpha'$ (and $\alpha$) phase in the temperature range 503–886.2 K:

$$\{H^\circ(T) - H^\circ(298.15\ \mathrm{K})\}/\mathrm{J\ mol^{-1}}$$
$$= 121.4700(T\ \mathrm{K^{-1}}) + 36.61196 \times 10^{-3}(T\ \mathrm{K^{-1}})^2$$
$$-39474.9.$$

The standard deviations are 127 J $\mathrm{mol^{-1}}$ for $SrSiO_3$, and 100 J $\mathrm{mol^{-1}}$ and 252 J $\mathrm{mol^{-1}}$ for the intermediate and high-temperature region of $Sr_2SiO_4$, respectively. The smoothed higher temperature thermodynamic quantities of $SrSiO_3$ and $Sr_2SiO_4$ are listed in Table 5. They have been calculated using the previously reported values for the enthalpies of formation of $SrSiO_3$ and $Sr_2SiO_4$, $-(1635.3 \pm 1.8)$ and $-(2305.7 \pm 2.2)$ kJ $\mathrm{mol^{-1}}$, respectively [13].

## 4. DISCUSSION

The low-temperature heat capacities and the high-temperature enthalpy increments have been measured using the same samples. As can be seen in Fig. 2 the two sets of data join smoothly at 298.15 K for $SrSiO_3$ as well as for $Sr_2SiO_4$. The low-temperature heat capacities measured by Weller and Kelly [3], in the temperature region 51–300 K are somewhat lower for $SrSiO_3$ and $Sr_2SiO_4$, the discrepancies increasing with temperature. The entropies calculated by these authors, $S^\circ$ (298.15 K) = (96.48 ± 0.85) J $\mathrm{mol^{-1}\ K^{-1}}$ for $SrSiO_3$ and (153.34 ± 1.26) J $\mathrm{mol^{-1}\ K^{-1}}$ for $Sr_2SiO_4$, are in reasonable agreement with the present results, being 0.9% higher and 1.4% lower, respectively. The slightly higher value for the entropy of $SrSiO_3$, compared with our value, can be explained by their estimated value for $S^\circ$(51 K) which is about 20% higher than our measured value.

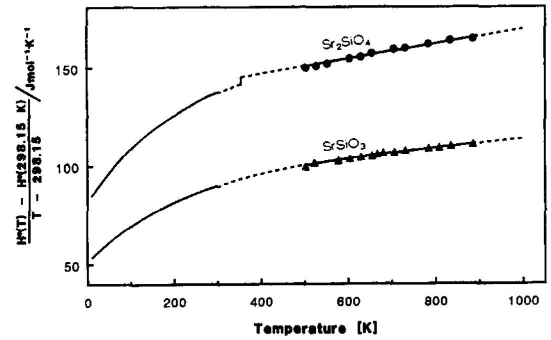

Fig. 2. The reduced enthalpy increments functions of $SrSiO_3$ and $Sr_2SiO_4$.

High-temperature enthalpy increments of these compounds have not been measured before, and only estimations by Spencer (quoted by Barin *et al.* [14]) are available in literature. These estimates are in good agreement with our measurements. For $SrSiO_3$ the estimated values in the temperature region 500–900 K are approximately 1.5% higher and for $Sr_2SiO_4$ approximately 0.7% lower than the values measured by us.

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