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Determination of temperature and enthalpy of melting of alkali disilicates by differential calorimetric analysis

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Alkali disilicates (lithium, sodium, potassium, rubidium, caesium) have been synthesized and the temperature, enthalpy and entropies of melting measured by differential calorimetric analysis. Unknown solid–solid transitions were detected for sodium and caesium disilicates. New X-ray diffraction patterns are given to characterize each disilicate.

1. Introduction

Equilibria as complex as those involved in the Earth sciences cannot easily be exhaustively investigated because the number of components, and hence the composition area, is very large. Their study requires some modelling which needs information about simple systems. At this stage, two kinds of thermodynamic data are needed.

(a) Thermodynamic data of mixing are very scarce but, generally speaking, do not strongly affect the results for multicomponent oxide systems. Many calculations safely assume ideal mixing.

(b) Thermodynamic data for pure components (standard values) are often missing, but are absolutely necessary.

We report results concerning temperatures, enthalpies and entropies of melting of $R_2Si_2O_5$ compounds (where R is an alkali metal) as well as some data on solid–solid transitions. These data are inherently interesting, but are also of interest because liquid disilicates can be considered as very simple magmatic melts for which many other measurements, such as viscosity or density, can be made.

2. Synthesis of samples

The main difficulty in handling these compounds is their hygroscopy which increases with the atomic number of the alkali element and becomes very cumbersome for caesium. It was necessary to perfect an anhydrous method of synthesis (and obviously of measurement). Consequently, we worked under dry atmosphere, acetone, rectified alcohol, or vacuum conditions at various stages.

Two synthesis procedures were tested for lithium disilicate. The humid one involved the preparation of gels from TEOS and alkali carbonates, the dry one from silica and alkali carbonates. Because the results were strictly equivalent, we used the dry method for the other disilicates because it is easier (silica, Merck Optipur; sodium carbonate, Merck Suprapur; potassium carbonate, Johnson Matthey Specpur; lithium, rubidium and caesium carbonate, Johnson Matthey Puratronic Gd1).

The dry method involves the following steps.

1. Drying the alkali carbonate and silica granules at 400–450 °C for 4 h and weighing.
2. Mechanical mixing and homogenization.
3. Desiccation and slow decarbonation between 400 and 800 °C.
4. At least two cycles of melting (≈4 h close to 1100 °C) -crystallization (≈8 h) -grinding to complete decarbonation and homogenization.
5. Finally, crystallization and slow cooling (50 °C, h^{-1}) to room temperature.

3. Characterization of disilicates

The composition and dryness of the products used to prepare the disilicates were verified by chemical analysis and differential thermal analysis. The compositions were controlled by mass balance and by chemical analysis with standard solutions (Aldrich). The differences between theoretical calculations and experimental determinations were less than 1.5% for lithium and sodium and less than 2.5% for the other compounds. After enthalpy measurements, the compositions of the samples used were re-analysed in the same way, leading to the same conclusions.

In order to estimate the loss of alkali metals due to evaporation or for any other reason, some specific experiments were performed under conditions

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favouring evaporation, e.g. very small sample size, large interface with air, and high temperature. Losses of alkalies up to 10% were observed which led to some phases richer in silica (glass and tetrasilicate), as verified by electron microprobe analysis. A lowering of the liquidus temperature was found due to the shift of the overall composition towards the disilicate–tetrasilicate eutectic. However, these effects were not observed in the compounds used for our calorimetric measurements. Therefore, we believe there was no alkali loss in our disilicates.

The different phases present in the samples were characterized before and after enthalpy measurements by optical methods (microscopic examinations and index determinations) and by X-ray ($\lambda CuK_{\alpha 1}$). The diffraction patterns were obtained by goniometry in the case of lithium disilicate which is not hygroscopic, and by photography in focalization chambers (Nonius and Seeman-Bohlin) in the other cases. This last technique allowed us to prevent reaction of the samples with water and carbon dioxide. The diffractograms (Table I) were calibrated using CaF_2 as an internal standard. When several phases were present their amounts were determined using reference curves obtained for mixtures of the same synthetic phases prepared separately in well-known proportions.

3.1. Lithium disilicate

The analysis showed the presence of some parasitic phases (cristobalite and metasilicate) even after very long annealing, synthesis from gels, or synthesis under hydrothermal conditions (1 kbar). The existence of such phases could be due to incongruent melting of lithium disilicate as mentioned by Kracek [1,2] or to the well-known metastability of high-temperature phases of silica. The presence of these phases (3.2 ± 0.7 % cristobalite and 4.8 ± 1.1% metasilicate in the samples used for the calorimetric measurements) should be taken into account in the determination of the enthalpy of melting. The diffraction pattern of lithium disilicate is in good agreement with the ASTM 17–447 standard.

3.2. Sodium disilicate

In addition to sodium disilicate, we detected some metasilicate (≈2 Wt %) but no cristobalite. The presence of metasilicate again could be due to the metastability of cristobalite (although it was not detected by X-ray) or to a small excess of sodium (0.4 wt %) due to loss of silica during preparation. The X-rays corresponding to the sodium disilicate are closer to those observed by Range and Willigallis [3] than by Willamson and Glasser [4].

3.3. Potassium disilicate

In the case of potassium disilicate, the X-rays given in Table I do not correspond to any value of the ASTM standards (ASTM 26-1331, 31-1076, 31-1077, 26-1463, 30-978 and 35-394). However, the results obtained in

TABLE I X-rays observed for alkali disilicates prepared in this work. Line 2: Grays analysis references. The number of crosses corresponds to increasing intensity of the corresponding X-rays

$Li_2Si_2O_5$ 7138-G	Li_2SiO_3 7174-G	Na_2SiO_3 6791-G	$Na_2Si_2O_5$ 6806-G	$Na_6Si_8O_{19}$ 6868-SB	$K_2Si_2O_5$ 7137-SB	$Rb_2Si_2O_5$ 7334-SB	$Cs_2Si_2O_5$ 8510-SB
× × 7.284	× × × 4.697	× × × 5.260	5.260	4.951	8.71	× 8.93	× 6.30
5.407	× 3.304	3.560	× × × 4.920	4.267	(7.02)	6.37	× 5.08
× × × 3.742	× × × 2.709	× × × 3.040	× × × 3.860	3.906	× 6.23	4.83	4.44
× × × 3.660	× 2.347	× 2.630	× × × 3.770	3.864	(5.73)	× 4.74	× 4.29
3.587	2.091	× 2.570	3.560	× × 3.791	3.97	× 4.72	4.18
2.945	2.081	2.410	3.480	3.484	× 3.77	× × 4.48	3.32
2.912	× × 1.776	2.310	× × × 3.300	× × 3.355	× × 3.075	4.29	× 3.08
2.710	× 1.657	× × 1.990	× 3.200	3.312	× × 3.015	× × 3.99	2.73
2.436	× × × 1.567	× 1.890	3.100	3.218	× 2.96	× × 3.86	2.54
2.389	× × × 1.561	× 1.840	× 3.040	3.113	× × 2.94	3.42	× 2.46
2.352	1.475	1.780	2.960	2.967	× 2.92	× × 3.18	2.34
2.292	1.409	× × 1.750	2.740	2.745	(2.87)	× × 3.10	2.22
2.056	1.375	1.650	× 2.640	× 2.650	2.86	3.05	× 2.15
2.013	1.348	1.540	2.570	2.541	2.77	× × 2.98	
× × × 1.966	1.300	× 1.520	× 2.530	× × 2.453	× 2.65	× 2.92	
1.870	1.297	1.460	× × 2.450	2.424	× 2.61	× 2.86	
1.847	1.255	× 1.450	× 2.410	2.393	× × 2.425	2.82	
× 1.829	1.250	× × 1.420	× 2.380	2.342	× × 2.065	× 2.79	
1.804		1.400	2.200	2.288	1.575	2.74	
1.796		1.315	2.140	2.244	1.475	2.68	
1.742		1.285	2.070	2.207	1.435	2.65	
1.652		1.269	2.000	2.149		2.54	
1.530		1.249	1.970	2.135		× 2.45	
1.519		1.207	1.950	2.102		× 2.41	
1.488		1.171	1.930	2.072		2.39	
1.474		× 1.148	1.870	2.009		2.32	
× × × 1.463		1.118	1.850	1.971		2.30	
1.439		–	1.770	× 1.949		2.28	
1.422			1.755	1.938		2.24	
–			–	–		–	

this work are the same for each method of synthesis used. The great care paid to avoid hydration of potassium disilicate leads us to question the ASTM standard.

3.4. Rubidium disilicate

The correspondence between our results and the ASTM standards (17-273, 21-750, 18-1121, 21-748, 17-274 and 21-749) is not complete; of the 51 lines observed, 19 cannot be identified. Some other phases could be present with the rubidium disilicate synthesized, but the literature is insufficient to confirm this interpretation or to identify the phases.

3.5. Caesium disilicate

The X-rays intensities are very weak although the time of exposure was long enough. The ASTM standards (19-317, 28-336 and 19-318) are dissimilar to our results for the same reason as for rubidium disilicate.

4. Calorimetric measurements

4.1. Apparatus and method

The enthalpies of transformation were determined by differential calorimetric analysis with the help of a commercial high-temperature Calvet-type calorimeter ($T < 1800$ K). The analyses were carried out on heating with heating rates between 350 and 390 K h^{-1}. The samples were contained in platinum crucibles under a pure argon atmosphere. The masses of the samples were about 100 mg. The calorimeter was calibrated under the same conditions with pure metals (99.99 mass %) : aluminium, T_{fus} = 933.3 K, H_{fus} = 10.79 kJ mol^{-1}; silver, T_{fus} = 1234 K, H_{fus} = 11.30 kJ mol^{-1}; copper, T_{fus} = 1356.6 K, H_{fus} = 13.05 kJ mol^{-1}; manganese, T_{fus} = 1517 K, H_{fus} = 12.06 kJ mol^{-1}; cobalt, T_{fus} = 1768 K, H_{fus} = 16.19 kJ mol^{-1}. These values were taken from Hultgren *et al.* [5]. The temperatures of solid transitions of manganese and cobalt were also used for the temperature calibration of the apparatus. Moreover, some enthalpy calibrations were performed by dropping small samples of US NBS α-alumina, the enthalpy of which is well known [6]. The two different methods yield similar enthalpic calibration data.

5. Results

5.1. Lithium disilicate

Fig. 1 shows a typical thermogram obtained for $Li_2Si_2O_5$. The small endothermic peak at about 1223 ± 3 K corresponds to a well-known solid-state transformation. The onset of melting is close to 1283 K; the melting temperature, defined as the intersection of the tangent to the thermogram at the inflection point with the base line, corresponds to 1311 ± 3 K in good agreement with the JANAF Thermochemical Tables value, 1307 ± 1 K [7]. The solid–solid transition temperature is somewhat higher (1223 K instead of 1209 K). According to Kracek [1, 2], the melting of lithium disilicate is not exactly congruent and it decomposes at 1306 K to give a liquid and Li_2SiO_3. However, the amount of Li_2SiO_3 is so small that we did not take it into account. The value of the enthalpy of solid-state transformation obtained in this work (0.9 ± 0.1 kJ mol^{-1}) agrees with the JANAF value (0.94 kJ mol^{-1}), but that of the enthalpy of melting is very much higher (82 ± 6 kJ mol^{-1} instead of 53.8 kJ mol^{-1}).

5.2. Sodium disilicate

Fig. 2 shows a typical thermogram for the heating of $Na_2Si_2O_5$. There are two overlapping endothermic peaks which are very difficult to separate from the enthalpic point of view. Their temperatures, are 1113 ± 3 K and 1147 ± 4 K, respectively. The second one corresponds to the melting of the compound, the first one to a solid-state transition not mentioned in the literature as far as we know. We did not observe the transitions at 951 and 980 K reported by Stull and Prophet [7]. However, the temperature of congruent melting of sodium disilicate agrees well with that of Stull and Prophet (1147 K). The separation of the two overlapping peaks by a method which uses the time constant of the calorimeter yielded 14.4 ± 2 and 34.0 ± 4 k $Jmol^{-1}$ for the enthalpy of solid-state transition and the enthalpy of fusion, respectively. The latter is in good agreement with the mean value of the JANAF Thermochemical Tables (35.5 kJ mol^{-1} [6] deduced from different data before 1959.

5.3. Potassium disilicate

The melting point of $K_2Si_2O_5$ is either 1311 or 1318 K according to Kracek *et al.* [8] and Bottinga [9],

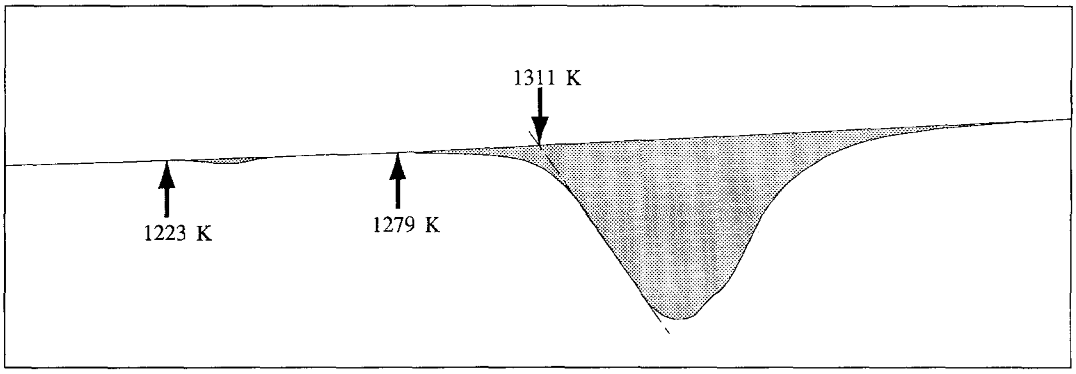

Figure 1 Typical thermogram obtained on $Li_2Si_2O_5$.

respectively. The thermogram obtained by DCA is shown in Fig. 3. There is a single endothermic peak after a long premelting phenomenon, starting at about 1186 K. Premelting decreases progressively during successive DCA made with the same sample. The melting point (1316 ± 3 K) agrees well with that given by Bottinga [9]. The corresponding enthalpy of fusion is 31.3 ± 3 kJ mol^{-1}. There are no data in the literature with which we can compare our result.

5.4. Rubidium disilicate

Fig. 4 shows a thermogram for $Rb_2Si_2O_5$ which melts congruently according to Alekseeva [10]. As with potassium disilicate, there is a single endothermic peak after a long premelting beginning at about 1273 K. The temperature of melting (1385 ± 4 K) is higher than that given by Alekseeva (1363 K). The enthalpy of fusion corresponds to 46.3 ± 4 kJ mol^{-1}. Again there are no data in the literature with which we can compare our result. We observed an exothermic peak at about 1010 K during successive DCA made on the same sample, and a drastic decrease in premelting. The enthalpy connected to this exothermic effect is about the same as for fusion. Such a non-equilibrium exothermic phenomenon can be easily explained by the lack of crystallization due to the high cooling rate between two successive analyses. The difficulty for such a liquid to crystallize is well known.

5.5. Caesium disilicate

The DCA thermogram (Fig. 5) shows endothermic phenomena at 1248 ± 5 and 1369 ± 5 K, respectively. The first one corresponds to a solid-state transition which is not mentioned in the literature, the second one to the congruent melting of the compound (1343 K according to Alekseeva [11]). The enthalpies

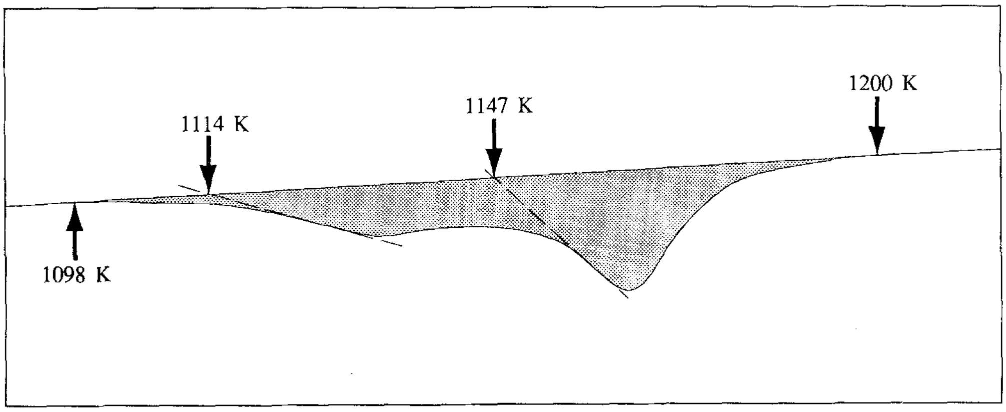

Figure 2 Typical thermogram obtained on $Na_2Si_2O_5$.

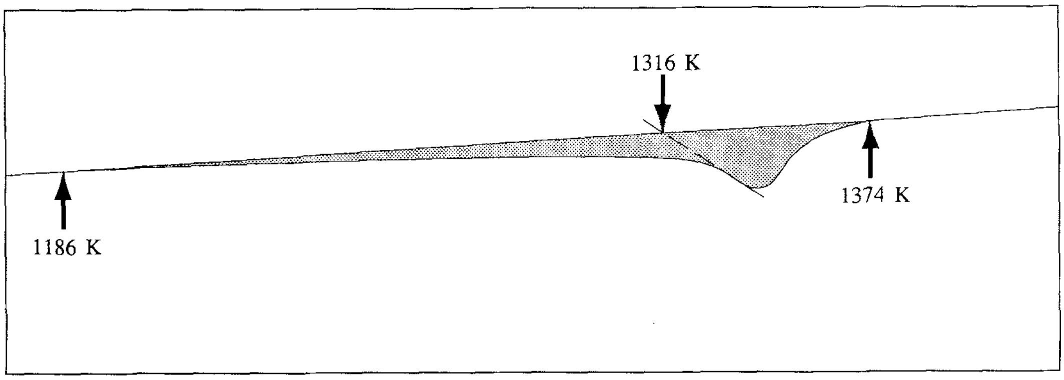

Figure 3 Typical thermogram obtained for the first DCA analysis on $K_2Si_2O_5$. The premelting phenomenon starting at 1186 K disappears progressively during successive analyses.

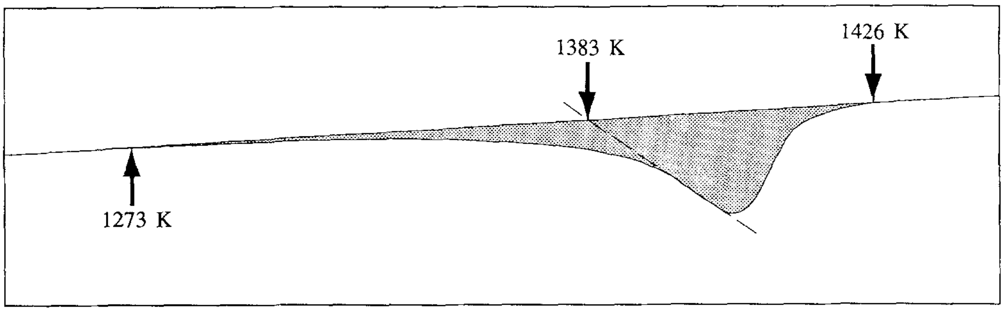

Figure 4 Typical thermogram obtained for the first DCA analysis on $Rb_2Si_2O_5$.

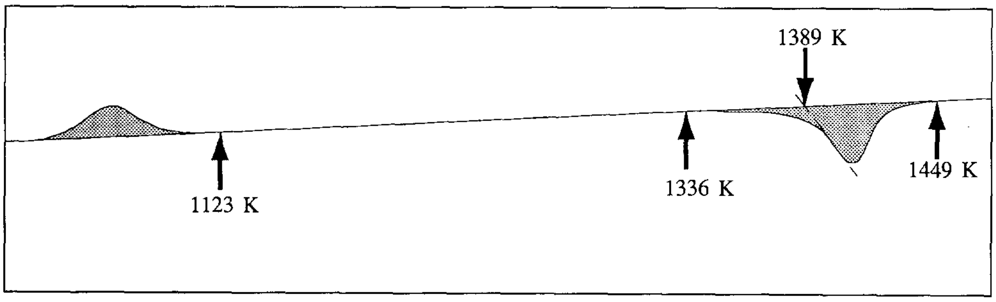

Figure 5 Typical thermogram obtained for the successive DCA analysis on $Rb_2Si_2O_5$ (after the first one, see Fig.4). The exothermic peak observed at about 1010 K is due to a non-equilibrium state obtained by rapid cooling after the first analysis.

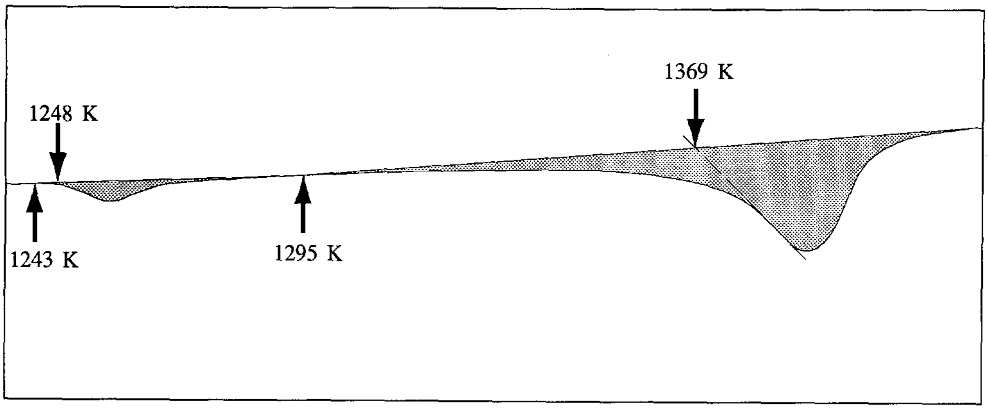

Figure 6 Typical thermogram obtained on $Cs_2Si_2O_5$.

TABLE II Change of state temperatures, enthalpies and entropies of alkali disilicates

Composition	T_{tr} (K)	H_{tr} (kJ mol^{-1})	T_{fus} (K)	H_{fus} (kJ mol^{-1})	S_{fus} (JK^{-1} mol^{-1})
$Li_2Si_2O_5$	1223 ± 3	0.9 ± 0.1	1311 ± 3	81.6 ± 6	62.2 ± 5
$Na_2Si_2O_5$	1113 ± 3	14.4 ± 2	1147 ± 4	34.0 ± 4	29.6 ± 3
$K_2Si_2O_5$			1316 ± 3	31.3 ± 3	23.8 ± 2
$Rb_2Si_2O_5$			1385 ± 4	46.9 ± 4	33.9 ± 3
$Cs_2Si_2O_5$	1248 ± 5	4.3 ± 0.4	1369 ± 5	49.0 ± 5	35.8 ± 4

are 4.3 ± 0.4 and 49.0 ± 5 kJ mol^{-1}, respectively. No corresponding data were found in the literature.

6. Conclusion

The results obtained in this work for the temperature and enthalpy of transition and melting of alkali disilicates (lithium, sodium, potassium, rubidium and caesium) are given in Table II. The higher the atomic number of the disilicates, the more sensitive it is to attack by water and carbon dioxide in the atmosphere, even at room temperature. Thus, their synthesis from stoichiometric mixtures of oxides and carbonates often does not lead to a single phase, but to a mixture of several silicates. However, the lack of reliable published X-ray data does not allow us to take into account the small gap between the composition observed and the stoichiometry.

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