Experimental determination of glass formation enthalpies in the system CaO-MgO-Al_2O_3-SiO_2 by isothermal drop calorimetry

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Enthalpies of vitrification are quantities required for a consistent thermodynamic description of multicomponent glasses. In this work, integral glass formation enthalpies of different compositions in a quaternary silicate system were measured at 1730K by inverse drop calorimetry using a differential high-temperature calorimeter. Samples with compositions corresponding to three invariant points in the quaternary system CaO-MgO-Al_2O_3-SiO_2 were selected and prepared from pure a-alumina, calcium carbonate, magnesium hydroxide carbonate, and silica glass. Enthalpy data were determined from the enthalpy difference $\Delta H(T_K - T_0)$ between room temperature T_0 and calorimeter temperature T_K. Enthalpies of vitrification were calculated from the difference of results for glassy samples and pure oxide mixtures with identical composition, respectively. Measurements for an individual composition were repeated at least 4 times. In order to establish an exact calibration, Pt samples with known mass were measured in alternation sequence with the glass or oxide samples. The results reflect the constitutional relations of the phase diagram CaO-MgO-Al_2O_3-SiO_2. They are discussed in terms of the structure of the individual crystalline reference state (c.r.s.).

1. Introduction

A large number of data in the thermochemistry of silicates is summarized in relevant standard works[1,2,3,4,5,6,7,8]. Available data are related to different technical areas, namely, geosciences, technology of glass and ceramic, metallurgy. Significant progress was reached for the calculation of thermodynamic equilibrium by computer software, e.g., F*A*C*T[9], HSC[10], MANLABS[11], MTDATA[12], THERDAS[13], THERMO-CALC[14]. The respective algorithm is mature and generally applicable to the calculation of thermodynamic data. But there are two insufficient points above all these algorithms to be taken as a basic tool. It is not suitable in the zone from the undercooled melt to the frozen status expect a few cases. In addition to this, there are only very few experimental data in multicomponent oxide systems. The main objective of the present investigation is the determination of the integral mixing- and devitrification enthalpy for the CaO-MgO-Al_2O_3-SiO_2 system, as well as the provision of systematic experimental data on the thermochemical behavior of this silicate system.

2. Experiment

In this investigation, compositions of samples corresponding to three invariant points in the quaternary system CaO-MaO-Al_2O_3-SiO_2 were selected in the phase diagram[15]. All glass samples were prepared by melting in a platinum crucible at temperature 1550 °C from pure α-alumina, calcium carbonate, magnesium hydroxide carbonate, and silica glass. After completion of the melting process, glasses were annealed at 800 °C for 4 hrs. and cooled at 3 K/min to room temperature. To confirm the glassy state, all samples were measured by X-ray powder diffraction analyses. Subsequently, compositions of all glasses were determined from X-ray fluorescence analyses.

Pure oxide mixtures with identical composition were prepared from pure α-alumina, silica glass, calcium oxide and magnesium oxide. Calcium oxide and magnesium oxide were prepared from calcium carbonate or magnesium hydroxide carbonate by decomposition, respectively. The oxide powders thus obtained were transferred in a desiccator to a glove box in which an atmosphere free from H_2O and CO_2 was maintained. From the fine powders of the component oxides, pure oxide mixtures with composition identical to the glass compositions were prepared in the glove box. The required amounts of the oxides were weighed out and mixed in a agate mixer mill and pressed in the form of pellets. In order to protect the oxide mixtures from H_2O and CO_2 in the air, they were taken individually from the glove box to the calorimeter with the aid of a sample holder closed at its ends.

Calorimetric measurements were made by the drop-mixing method. Glasses and pure oxide mixtures at room temperature were dropped into the calorimeter operating at 1730 K in which an identical composition was melted, and the enthalpy effects associated with the reactions occurring in the calorimeter were measured. Details of the method of measurement have been reported before[16 17].

All calorimetric experiments were performed in a differential high-temperature integrated heat-flux calorimeter MultiHTC (Setaram). The central part of the calorimeter is represented by the grooved tube shown in Fig. 1, made from recrystallized alumina.

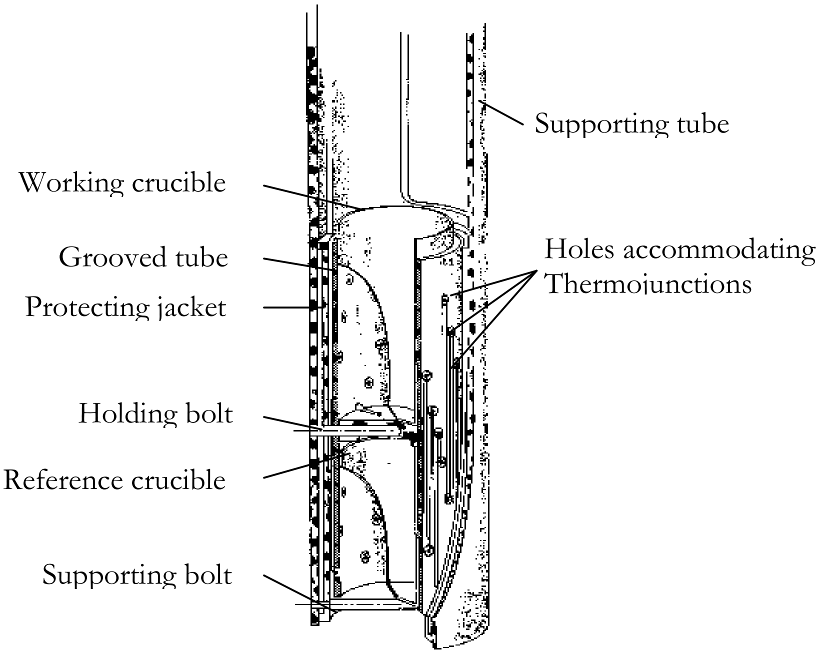

Fig. 1. Diagrammatic representation of the detector employed in the Multi-Detector High-Temperature Calorimeter (Setaram)

A disc-shaped piece of alumina fixed in the middle of the grooved tube by an alumina bolt divides the space enclosed by the tube into two halves. The upper half, acting as the "working cell" of the differential calorimeter, contains the "working crucible" in which the sample reacts during a calorimetric measurement. The lower half represents the "reference cell" of the calorimeter and holds the "reference crucible". In the calorimetric measurements performed in this study, a platinum crucible was located in the working crucible in order to protect the alumina working crucible from attack by the samples.

The calibration of the calorimeter was performed by dropping spheres of platinum at room temperature into the calorimeter operating at the measurement temperature. The enthalpy effects in the calibrations were calculated using Kelley's enthalpy data for platinum[18].

3. Results and discussion

By X-ray diffraction, none of the glass samples showed crystallization peaks, hence all were X-ray amorphous. Compositions of glass samples were determined by X-ray fluorescence analyses and given in table 1. The composition in terms of the crystalline (equilibrium) reference state (c.r.s.) is also given.

Tab. 1. Composition of glasses A to C in wt. % in terms of oxides and of the c.r.s.

	CaO	**MgO**	**Al_2O_3**	**SiO_2**	**cr**	**en**	**fo**	**wol**	**di**	**An**	**ak**
A	23.3	10.9	15.4	50.4	0.21	0.60			57.21	41.98	
B	31.3	8.1	16.8	43.8			0.04		1.62	45.79	52.55
C	24.6	4.5	12.6	58.3	17.81			23.63	24.17	34.39	

According to the phase diagram[15] , the c.r.s. corresponding to the composition of glass A comprises anorthite (an) and diopside (di). For glass B, it is anorthite (an) and akermanite (ak), for glass C cristobalite (cr), anorthite (an), wollastonite (wol) and a solid solution with end members anorthite (an) and diopside (di).

Calorimetric measurements were carried out in the temperature range from room temperature T_0 (293 K) to the calorimetric temperature T_K (1730 K). Enthalpy data were determined from the enthalpy difference $\Delta H(T_K - T_0)$ between room temperature and calorimeter temperature T_K.

$$\begin{array}{llll}
\text{glass } (T_0) & \rightarrow & \text{melt } (T_K) & \Delta H_T \text{ (glass)} \\
\text{oxides}^* (T_0) & \rightarrow & \text{melt } (T_K) & \Delta H_T^* \text{ (oxides)} \\
n \cdot SiO_2 \text{ (cr)} & \rightarrow & n \cdot SiO_2 \text{ (glass)} & n \cdot H^{vit} (SiO_2) \\
\hline
\text{oxides } (T_0) & \rightarrow & \text{glass } (T_0) & \Delta H_{ox}^f \text{ (glass)}
\end{array}$$

All experimentally determined enthalpies for glass samples and for the pure oxide mixture of the composition A are given in table 2. The formation enthalpies of the c.r.s. according to table 1 and the enthalpies of vitrification calculated from the difference are also given.

Tab. 2. Enthalpy increment ΔH_T , ΔH_T^* measured by dropping glass samples and oxide mixtures (incl. the amount n of SiO_2 as silica glass) into the calorimeter from room temperature (T_0 = 293 K) to the calorimetric temperature (T_K = 1730 K). The calculated ΔH_T (c.r.s.) to form a melt at T_K from the crystalline reference state according to table 1 is also given as the calculated enthalpy of fusion H^{fus} at T_K from these crystalline phases. The enthalpy of vitrification H^{vit} is calculated.

Samples	ΔH_T , ΔH_T^* [J/g] number of samples(n)	ΔH_T (c.r.s.) [J/g]	H^{vit} [J/g]	H^{fus} [J/g]
Glass A	2064 ± 36 (7)	2246	182	609
Oxide A	1509 ± 29 (7)			
Glass B	1796 ± 49 (7)	2179	383	603
Glass C	1763 ± 32 (7)	2152	389	513

H^{vit} (SiO_2) from the literature[4] (6.9 kJ/mol) was used to derive the formation of glass from the oxides ΔH_{ox}^f (glass) from the directly measured enthalpy ΔH_T^*(oxides). With respect to the formation enthalpy of the crystalline reference state (c.r.s) according to table 1 we can compare the calculated value H^{vit} for composition A given in table 2 with the following scheme:

oxides (T_0) → glass (T_0) ΔH_{ox}^f (glass)
oxides (T_0) → c.r.s. (T_0) ΔH_{ox}^f (c.r.s.)
c.r.s. (T_0) → glass (T_0) $\Delta H^{vit} = \Delta H_{ox}^f\,(\text{glass}) - \Delta H_{ox}^f\,(\text{c.r.s.})$

For the composition of glass A we have from the experiment ΔH_T(glass), ΔH_T^*(oxides) and from calculation according to the composition of the mixture of the oxides the amount of $n \cdot H^{vit}(SiO_2)$ and ΔH_{ox}^f (c.r.s.). Thus we get for ΔH_{ox}^f (glass) 613 J/g and for the formation enthalpy ΔH_{ox}^f (c.r.s.) of the cristalline reference state phases 541 J/g. The difference shows an enthalpy of vitrification ΔH^{vit} for composition A of 72 J/g with an uncertainty of ± 46 J/g by experimental method.

4. Summary

The present experimental study shows that the drop calorimetric method is a powerful tool in the determination of vitrification enthalpies. The comparison between the values derived from extrapolation of the crystalline reference state phases to the measuring temperature and the directly measured values by oxide mixtures shows the requirement of an intensive experimental work on the measurement of vitrification enthalpies of the crystalline reference state glasses and their mixtures. The aim is to improve the model of the constitutional crystalline phases for the amorphous region of multicomponent systems. The method is applied to compositions of 3 invariant points in the system CaO-MgO-Al_2O_3-SiO_2 yielding values with amount from 30 to 76 % of the enthalpies of fusion.

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